DISTRIBUTION OF ELEMENTS AMONG FELDSPARS, MICAS, AND EPIDOTE IN SOME METAMORPHIC ROCKS NEAR BANCROFT, ONTARIO

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ABSTRACT

The Oak Lake-Whetstone Lake area lies within the Haliburton-Bancroft region of the Grenville Province of the Canadian Shield. It is underlain by a great variety of metasedimentary and metavolcanic rock types which range in grade from the garnet zone to the biotite-garnet-sillimanite zone of the almandine amphibolite facies. The present research is particularly concerned with the study of equilibria involving: 1) muscovite + biotite, 2) plagioclase + epidote, 3) K-feldspar + plagioclase, and 4) muscovite + two feldspars.

1. The partitioning of Li, Mn, Na, Ti, total Fe and Mg between muscovite and biotite shows that equilibrium has been approached in the distribution of these elements. Muscovite and phengite, supposedly a lower grade variety of muscovite, occur over the whole range of metamorphic conditions and two trends have been recognized, corresponding to the assemblages: phengite-biotite and muscovite-biotite. No relationship between composition and metamorphic grade has been found in micas, and the bulk composition of the host rock seems to play a major role, obscuring the effect of increasing temperature.

2. A study of composition of zoned plagioclases coexisting with epidotes (sometimes zoned) has revealed that in epidote-

bearing assemblages, the plagioclase is An-rich and the An content increases toward the border of the grains. The zoning occurring in epidote is defined by an increase in the pistacite component from the core toward the rim. A series of reactions involving plagioclase + epidote has been suggested on the basis of textural and chemical data. As a result of these reactions, the Al-component of the epidote reacts to produce An-molecules and the epidote becomes enriched in the Fe component. The CO_2/H_2O ratio in the vapor phase and the Fe^{2+}/Fe^{3+} ratio in the minerals seems to affect the equilibrium conditions of the suggested reactions.

3. The distribution of albite between two feldspars is in agreement with the results obtained by Smith (1967) for the middle almandine amphibolite facies. The scattering of data has been attributed to exsolution of albite from microcline. This is suggested by the frequent occurrence of discontinuous normal zoning and sodic rims in plagioclase which are particularly developed at the contact with microcline.

4. The distribution of Na and K between muscovite and plagioclase is affected by the X_{Fe} ratio in muscovite and the An content of plagioclase. Other compositional variables may possibly influence the distribution.

I INTRODUCTION

General Geology

The Oak Lake-Whetstone Lake area lies within the Haliburton-Bancroft region and includes part of the townships of Belmont, Lake, Methuen and Wollaston. The area lies within the Grenville Province of the Canadian Shield and the bed rocks are of Precambrian and Paleozoic age. The location of the samples studied and the geology of the area are shown in the included map. The following two Precambrian formations have been distinguished (Hewitt, 1960, 1962; Heidecker, 1963; Laakso, 1968):

1) Oak Lake formation which extends from southern Methuen into Lake Township, toward Tangamong Lake and the Ridge Dome; the lithology is complex and a great variety of metasedimentary and metavolcanic rocks is present. Above this formation lies the:

2) Vansickle formation which consists mostly of interbedded marbles and schists with amphibolites and quartzites. An unconformity between the two formations is marked by the presence of a conglomerate.

The rocks have been intruded by igneous rocks of a wide range of composition. The oldest intrusives are basic, diorite and gabbro, ranging from peridotite to quartz-diorite (Horse Lake and Twin Lake diorites). The nepheline-syenite of Blue Mountain, which has been intruded and replaced by pink syenite, is younger in age. The latest intrusive rocks belong to the granite group.

Most of the specimens studied in the present research belong to the Oak Lake formation.

Metamorphic Grade

The metamorphic grade of these rocks changes widely across the area. Carmichael (1968, 1970) carried out a detailed study of pelitic assemblages in the Whetstone Lake area and determined a succession of metamorphic zones on the basis of changes in mineral compatibilities. By plotting the reactant and the product assemblages on a map, Carmichael defined a series of isograds which mark the transition between the following zones of increasing metamorphic grade: garnet, staurolite-biotite, kyanite-biotite, sillimanite and sillimanite-garnet-biotite. Each of these zones has been named after the product assemblage of the reaction that defines its lower boundary. Agreement has been found between the results of the present research and the isograds as defined by Carmichael which have been tentatively drawn in the lower part of the area on the basis of the data available (see geologic map). The lack of pelitic schists in the southwestern side of Oak Lake does not permit one to define the boundary between the sillimanite and sillimanite-garnet-biotite zones.

The assemblage microcline-sillimanite, which has been found at Blue Mountain and at Coe Hill suggests the existence of a K-feldspar-sillimanite isograd to the north and west of the map area.

Purpose of the Present Study

The great variety of rock composition and metamorphic grade makes the Oak Lake-Whetstone Lake area particularly suited for a detailed study of mineral equilibria. In the following chapters some possible reactions and equilibria involving muscovite + biotite, plagioclase + epidote, K-feldspar + plagioclase and muscovite + two feldspars will be discussed in detail. The effects produced by bulk composition and metamorphic differences on the above equilibria will be particularly stressed.

Methods of Analysis

The specimens studied in this research were collected during the summers 1966 and 1967. In the first year, the field work was also extended to the townships of Chandos, Limerick and Marmora and the Oak Lake-Whetstone Lake area was chosen after an attentive study of metamorphic grade and mineral associations. The field work in the summer of 1967 was exclusively carried out in this area.

The samples were selected after a careful examination of thin sections to avoid inhomogeneity and retrograde phenomena. The minerals were concentrated by means of a Frantz isodynamic separator and heavy liquids of appropriate density and the solutions obtained were analyzed with a Techtron model AA_4 atomic absorption spectrophotometer for the following elements: Na, K, Ca, Li, Mn, Fe, Mg and Sr. The Al and Ti content of micas and the composition of epidotes, zoned plagioclases and some K-feldspars were determined with an A.R.L. electron microprobe. More detailed information on the analytical methods is given in the Appendix.

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II THE MICA MINERALS

Introduction

Butler (1967) in his study of coexisting micas in metamorphic rocks of the Moine Series, Scotland, of metamorphic grade ranging from the biotite to the staurolite zone, recognizes that there are systematic variations in composition of the micas which can be related to variations in: a) bulk chemical composition and mineral paragenesis; and b) grade of metamorphism. The variation in mica composition due to the effect of the mineral paragenesis is often greater than the variation due to the grade of metamorphism and Butler could observe the existence of compositional trends in micas only after grouping them on the grounds of the presence or absence of epidotes and states that, "if two micas from different groups are compared, the trends are sometimes obscured or reversed".

A great variability of bulk composition and mineral paragenesis over a wide range of metamorphic grade makes the Oak Lake-Whetstone Lake area suitable for a study of mica equilibria.

The present report includes chemical analyses of 28 samples of muscovite and 38 of biotite. Special attention will be given to 26 pairs of micas occurring over a metamorphic grade ranging from the garnet zone to the sillimanite - K feldspar zone of the almandine amphibolite facies.

Mineral Assemblages and Chemical Analyses

Micas have been found in the following mineralogical assemblages:

1. muscovite + biotite + chlorite + plagioclase + quartz + calcite (± epidote ± garnet).
2. muscovite + biotite + epidote + plagioclase + quartz + calcite (± microcline ± garnet ± hornblende).
3. muscovite + biotite + garnet + plagioclase + quartz (± kyanite ± staurolite).
4. muscovite + biotite + plagioclase + microcline + sillimanite ± quartz (±garnet).
5. biotite + plagioclase + quartz (±garnet ± epidote ± hornblende ±calcite ± scapolite).
6. muscovite + plagioclase + microcline + quartz (± garnet ±sillimanite).

The results of the analyses are presented in tables 1 and 2.

On a comparison of the chemical data of coexisting micas, biotites appear to contain more total iron (expressed as Fe_2O_3), MgO, MnO, TiO_2 and Li_2O and less Na_2O, K_2O and Al_2O_3 than the coexisting muscovites. CaO shows a slight

TABLE 1

Muscovite Analyses

sample number	Na_2O	K_2O	CaO	MgO	Fe_2O_3	MnO	Li_2O	Al_2O_3	TiO_2
9	.88	10.5	.24	1.2	4.1	.008	.004	n.d.*	n.d.
28	.94	9.8	.28	.7	2.1	.008	.003	n.d.	n.d.
41	.52	10.6	.10	1.0	1.2	.004	.005	38.0	.2
89	.49	10.2	.16	.4	1.4	.004	.002	37.9	1.2
91	.31	11.0	.23	1.2	3.7	.023	.009	n.d.	n.d.
102	.39	10.9	.23	1.3	4.7	.007	.005	n.d.	n.d.
162	.25	11.1	.19	1.3	5.0	.018	.010	29.9	1.1
196	.25	10.7	.27	1.3	4.5	.019	.008	30.6	.5
212	.29	10.8	.42	1.4	5.2	.018	.006	30.6	1.2
229	.35	11.0	.36	1.6	4.9	.021	.007	30.9	1.2
240	.61	10.7	.21	1.1	4.9	.015	.022	n.d.	n.d.
277	.42	11.0	.21	1.6	5.2	.026	.012	n.d.	n.d.
282	.60	10.0	.48	1.7	5.6	.049	.015	29.8	.5
330	.39	10.9	.18	1.7	5.7	.044	.016	31.3	1.0
369	.67	10.5	.30	1.4	5.2	.035	.015	n.d.	n.d.
370	.34	11.1	.08	.8	5.1	.026	.024	n.d.	n.d.
375	.61	10.7	.19	.7	2.6	.007	.009	n.d.	n.d.
378	.56	10.8	.23	1.7	4.9	.016	.014	31.4	1.4
400	.62	9.9	.23	1.0	3.3	.007	.009	n.d.	n.d.
407	.41	11.0	.07	1.2	4.8	.011	.008	n.d.	n.d.
411	.67	10.7	.48	1.1	4.3	.043	.006	n.d.	n.d.
419	.32	10.8	.17	1.3	5.6	.021	.011	29.7	.7
425	.39	10.8	.11	1.5	6.0	.012	.014	n.d.	n.d.
428	.67	10.3	.23	1.0	3.9	.009	.003	n.d.	n.d.
431	.40	11.1	.18	1.5	5.2	.012	.014	31.5	.7
436	1.18	10.7	.05	.5	1.6	.002	.001	38.4	.4
456	.25	10.9	.11	1.5	5.4	.403	.098	n.d.	n.d.
464	.60	6.5	.18	.9	3.7	.026	.026	n.d.	n.d.

* not determined

TABLE 2

Biotite Analyses

sample number	Na_2O	K_2O	CaO	MgO	Fe_2O_3	MnO	Li_2O	Al_2O_3	TiO_2
277	.14	9.8	.10	13.0	15.4	.39	.029	n.d.*	n.d.
282	.08	9.8	.17	12.4	15.2	.82	.041	15.6	1.5
309	.16	8.9	.21	8.8	20.4	.25	.018	15.4	2.2
330	.08	9.7	.13	12.7	13.3	.73	.029	15.4	1.9
369	.27	9.5	.25	11.3	18.8	.62	.056	n.d.	n.d.
375	.14	9.6	.07	10.9	19.3	.18	.056	n.d.	n.d.
378	.15	9.8	.23	13.4	13.4	.35	.037	16.4	2.0
382	.23	9.5	.22	15.2	14.4	.26	.027	15.1	1.7
400	.18	9.2	.17	9.8	21.6	.13	.029	n.d.	n.d.
407	.13	9.6	.22	9.5	19.7	.16	.036	n.d.	n.d.
411	.14	9.2	.19	8.5	21.1	.43	.027	n.d.	n.d.
414	.19	9.1	.14	3.5	31.8	.41	.018	n.d.	n.d.
419	.09	9.3	.15	8.5	21.7	.43	.041	15.3	2.0
425	.13	8.9	.37	12.0	18.8	.23	.059	n.d.	n.d.
428	.16	9.4	.26	10.3	19.1	.10	.028	n.d.	n.d.
431	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	15.1	2.5
436	.25	8.9	.08	7.5	24.1	.02	.008	17.7	1.6
461	.13	9.4	.08	12.5	18.5	.38	.74	14.6	2.3
464	.12	9.2	.12	10.1	18.8	.51	.059	n.d.	n.d.

* not determined

TABLE 2

Biotite Analyses

sample number	Na_2O	K_2O	CaO	MgO	Fe_2O_3	MnO	Li_2O	Al_2O_3	TiO_2
9	.16	9.4	.07	10.5	19.3	.16	.023	n.d.*	n.d.
25	.11	9.0	.17	7.6	24.8	.33	.021	n.d.	n.d.
28	.18	9.6	.24	5.8	26.8	.13	.017	n.d.	n.d.
41	.03	10.0	.01	13.5	12.8	.17	.054	20.5	.4
42	.52	9.2	.04	9.3	21.0	.09	.024	n.d.	n.d.
52	.17	9.5	.30	11.9	16.4	.19	.015	n.d.	n.d.
89	.14	9.1	.17	5.3	25.6	.12	.012	18.8	3.6
91	.13	9.7	.08	14.5	12.8	.71	.051	n.d.	n.d.
95	.49	9.3	.20	9.4	21.8	.17	.022	n.d.	n.d.
102	.11	9.5	.18	10.3	19.1	.11	.019	n.d.	n.d.
162	.10	9.4	.22	9.0	19.8	.36	.034	17.6	2.4
196	.12	9.5	.22	11.3	14.6	.35	.023	16.4	1.5
197	.16	9.6	.23	9.8	18.8	.32	.019	15.8	1.9
199	.12	9.0	.38	10.6	20.6	.24	.021	16.9	2.0
212	.11	9.9	.23	10.3	18.3	.34	.029	16.7	2.5
229	.15	9.7	n.d.	13.2	14.2	.38	.068	16.6	2.5
240	.05	9.1	.10	7.5	23.8	.57	.091	n.d.	n.d.
255	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	15.6	1.6
272	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	15.9	1.8

preference for muscovite, but some biotites (i.e. 89, 162, 407, 425 and 436) are richer in CaO than the muscovites occurring with them.

Muscovites

The chief compositional variables for muscovites are (from table 1): Fe_2O_3 (from 1.2 to 6%), Al_2O_3 (from 29.7 to 38.4%), MgO (from .40 to 1.7%) and TiO_2 (from .20 to 1.4%). Al_2O_3 and Fe_2O_3 + MgO vary inversely, the muscovites having smaller amounts of Al_2O_3 being richer in Fe_2O_3 + MgO and viceversa.

The Al-poor micas are slightly colored in thin sections and show a faint pleochroism. Optical properties ($2V<40^{\circ}$, optic plane $\perp$ 010, absorption :$X<Y=Z$, pleochroic colors :X= colorless and Y=Z=pale green, pale brown or yellow) indicate either ferromuscovite or phengite but chemical data suggest phengite.

Previous work on phengites

Winchell (1927,1949) recognized two phengite end members:

1) picrophengite = $K\ Mg_{0.5}\ Al_{1.5}\ Si_{3.5}\ Al_{0.5}\ O_{10}\ (OH)_2$ and
2) ferrophengite = $K\ Fe^{2+}_{0.5}\ Al_{1.5}\ Si_{3.5}\ Al_{0.5}\ O_{10}\ (OH)_2$.

More recently, Kanehira and Banno (1960) have defined these micas in terms of four end members:

1) Muscovite = K Al_2 Si_3 Al O_{10} $(OH)_2$

2) Ferrimuscovite = K $Fe^{3+}_{0.5}$ $Al_{1.5}$ Si_3 Al O_{10} $(OH)_2$

3) Phengite = K $(Mg, Fe^{2+})_{0.5}$ $Al_{1.5}$ $Si_{3.5}$ $Al_{0.5}$ O_{10} $(OH)_2$ and

4) Ferriphengite = K $(Mg, Fe^{2+})_{0.5}$ $Fe^{3+}_{0.5}$ Al $Si_{3.5}$ $Al_{0.5}$ O_{10} $(OH)_2$.

Schaller (1950) and Foster (1956) discussed chemical composition of members of this group and indicated that variation, although incomplete, is between a tetrasilicic end member (e.g. celadonite - K Fe^{2+} Fe^{3+} Si_4O_{10} $(OH)_2$) and a trisilicic end member (e.g. muscovite). Ferrous iron and Mg constitute a diadochic pair, likewise Fe^{3+} and Al. Foster (1956) showed that this series, of which muscovite is the trisilicic end member, is characterized by a gradual shift in the seat of the inherent unit charge from the tetrahedral layers to the octahedral layer.* This shift is brought about by the replacement of octahedral aluminum by bivalent cations, usually Fe^{2+} and Mg. As this replacement is ion for ion, and the total number of octahedral cations remains the same, there is deficiency in positive octahedral charges necessary to neutralize the anions associated with this layer and it develops

* In theoretical formulae for dioctahedral and trioctahedral micas, the entire composite - layer charge originates in the tetrahedral layers owing to substitution of 1/4 of the Si by Al; the octahedral layer is neutral. (Foster, 1960)

a negative charge, this charge being the greater, the greater the replacement of trivalent cations by bivalent cations. Coincident with this replacement and the development of a negative charge on the octahedral layer, there is an equivalent decrease in the negative tetrahedral charge, due to an increase in Si and a decrease in tetrahedral Al. Replacement of half the octahedral trivalent cations by bivalent cations produces the tetrasilicic end member, in which all the inherent unit-layer charge is on the octahedral layer, and the tetrahedral layers, completely filled by Si, are neutral. Replacement of Ti^{4+} for Al^{3+} in octahedral coordination can partly compensate the bivalent ions - Al^{3+} substitution.

In trioctahedral micas such as phlogopite, the higher octahedral charge produced by the substitution of Al^{3+}, Fe^{3+} and Ti^{4+} for Mg (and Fe^{2+}) is compensated in two ways:

1) by an equivalent increase in the negative tetrahedral charge by substitution of Al for Si; or

2) by nonoccupancy of octahedral sites (the negative charges associated with these sites being then available to neutralize the additional positive charges carried by the proxying cations).

Lambert (1959) recognized that, in Moine series rocks of the greenschist facies (Scotland), white micas change from phengitic to muscovitic compositions with increasing metamorphic grade. Ernst (1963) stated that the reaction can be represented in the 7 component system, $K_2O - Al_2O_3 - Fe_2O_3 - FeO - MgO - SiO_2 - H_2O$ - and, "because ferric iron and aluminum constitute a diadochic pair (R^{3+}) for the minerals considered, and Fe^{2+} and Mg likewise are mutually substitutional (R^{2+}), the reaction can be written more simply in terms of 5 components:

1. $8\ K\ R_{1.5}^{3+}\ R_{0.5}^{2+}\ Si_{3.5}\ R_{0.5}^{3+}\ O_{10}\ (OH)_2$ (phengite) $+\ R_5^{2+}\ R^{3+}\ Si_3\ R^{3+}\ O_{10}\ (OH)_8$ (chlorite) $=\ 5\ K\ R_2^{3+}\ Si_3\ R^{3+}\ O_{10}\ (OH)_2$ (muscovite) $+\ 3\ K\ R_3^{2+}\ Si_3\ R^{3+}\ O_{10}\ (OH)_2$ (biotite) $+\ 7\ Si\ O_2 + 4\ H_2O$

Van der Plas (1959) introduced another possible reaction occurring during the metamorphism of biotite-rich granitic rocks. The rare occurrence of biotite in the derived phengitic gneisses has been explained by the following reaction:

2. biotite + 3 sericite (muscovite) + 2 microcline + 3 quartz + 2 H_2O = 6 phengite

from which the Mg and Fe content of the phengite could be derived from original biotite.

The results obtained by Lambert have been confirmed by Butler (1967) who found a general increase of Al content in tetrahedral and octahedral coordination in muscovite with increasing metamorphic grade, but he states (p. 247) that, "the muscovites from rocks without epidote show a rather better correlation of increasing Al content with increasing grade of metamorphism than the muscovites from epidote-bearing rocks". The experimental data of Velde (1964) indicated that iron and magnesium rich phengitic micas are stable at low temperature and high pressure, and that the range of composition of the dioctahedral micas decreases and converges on the muscovite (sensu stricto) composition as the temperature increases, due to the breakdown of phengite into aluminous muscovite + biotite, feldspar and quartz.

Butler (1967) discussing the "apparent absence of aluminous muscovite from low temperature metamorphic environments", advanced the possibility that a decreased stability and range of solid solution of the associated minerals, such as biotite, almandine, staurolite, etc... allows Fe and Mg to enter the structure of muscovite while at higher temperatures the structure of these minerals is able to accept ions which at low temperature have to enter muscovite.

Relationship of phengite to metamorphic grade in the study area

In the Oak Lake-Whetstone Lake area, phengitic micas have been found occurring in assemblages of a metamorphic grade as high as the sillimanite-garnet-biotite zone; but aluminous muscovite may be present in lower grade assemblages proving that the occurrence of either mineral is controlled by the bulk composition and mineral paragenesis. In this regard, let us compare muscovites 196 and 436 which lie above and below the sillimanite-garnet-biotite isograd. The two samples have the following parageneses: (196) = muscovite - biotite - plagioclase - microcline - quartz (epidote), and (436) = muscovite - biotite - plagioclase - almandine - staurolite. Ms 436 contains 38.4% Al_2O_3, 1.6% Fe_2O_3 and .48% MgO, while Ms 196 has a higher Fe_2O_3 and MgO content (respectively 4.5 and 1.3%) and a lower Al_2O_3 (30.6%). The presence of Fe-rich minerals such as garnet and staurolite in sample n° 436 decreases the affinity of Muscovite for Fe (and Mg) while higher grade micas not coexisting with such minerals are still phengitic in composition.

Samples n° 41 and 89 which belong to the highest metamorphic grade (sillimanite - K-feldspar) contain Al-rich muscovites. It can then be concluded that the presence of muscovite or phengite in the area studied is not a simple function of the metamorphic grade, as generally recognized, but is highly affected by the bulk composition of the host rock.

Biotites

Previous work

According to Winchell (1951), the composition of biotite is expressed in terms of the following end members, if Fe^{3+} may be included in Al and the amount of Ti-biotite molecule may be disregarded:

Phlogopite: $K_2Mg_6Al_2Si_6O_{20}(OH)_4$
Eastonite: $K_2Mg_5Al_4Si_5O_{20}(OH)_4$
Annite: $K_2Fe_6Al_2Si_6O_{20}(OH)_4$ and
Siderophyllite: $K_2Fe_5Al_4Si_5O_{20}(OH)_4$

Variation in the composition of biotite with grade of metamorphism has been demonstrated from a number of localities. Barth (1936) found that the biotite in the higher grade rocks of Dutchess County has a lower iron content than those in the lower grade rocks. Engel and Engel (1960) found a decrease in Mn, Fe^{2+} and Fe^{3+} and an increase in Ti, Mg, Ba, Cr and V with increasing metamorphic grade in biotites of the major Adirondack paragneiss. Lambert (1959) in a study of biotites from Moine rocks of the Morar district, Inverness-shire, showed an increase of Mg content with increasing grade, but recognized that the composition of the host rock plays a significant part in the MgO content of biotite. De Vore (1955) has observed an increase in the content of Fe^{2+} and Mn with increasing metamorphic grade in biotites from various localities. The same trend has been recognized by Miyashiro (1958) who also showed that the biotites in the pelitic rocks of the higher zones of the central Abukuma plateau, Japan, have a higher Ti and a lower Mn content than those of the intermediate zone.

The effect of the mineral paragenesis on the composition of metamorphic biotites has been discussed by Butler (1967) who observed that biotites coexisting with garnets have a higher Mg-content due to the preferred entry of Fe into garnet.

Hayama (1964) found that with increasing metamorphic grade, biotite becomes richer in Al_2O_3 with subordinate increase of TiO_2, and in the highest grade of metamorphism, the increase of TiO_2 and the decrease of Al_2O_3 are clearly recognized. He considers three members of the biotite group: 1) Ferromagnesian biotite, 2) Aluminous biotite and 3) Titanobiotite and, with grade increasing from epidote-amphibolite to granulite facies, biotite should change in the order from 1 $\rightarrow$ 2 $\rightarrow$ 3; but he states that Mg and Fe contents of biotite are largely controlled by the chemical composition of its host rock.

Relationship to metamorphic grade in the study area

In the biotites of the Oak Lake-Whetstone Lake area, the chief compositional variables are total iron (expressed as Fe_2O_3) (from 12.8 to 26.8%), MgO (from 3.5 to 14.4%), TiO_2 (from .4 to 3.6%) and Al_2O_3 (from 14.6 to 20.5%). From the chemical data of table 2, the following observations can be made:

1) biotites coexisting with muscovites have a higher Al_2O_3 content than biotites coexisting with phengites (see biotites n° 41, 89 and 436).

2) due to the different mineralogical parageneses it is not possible to recognize any trend in the variation of MgO and total iron (as Fe_2O_3) with metamorphic grade.

3) biotites n° 28, 89, 197, 199, 240, 411 and 436 coexist with garnet, but do not show any marked increase in MgO with respect to biotite not coexisting with it. The reason could be found in the presence of other Fe and Mg-bearing minerals (such as chlorite, epidote, hornblende, muscovite and staurolite) in the above mentioned samples which most probably upset the trend observed by Butler (1967).

In this regard, let us consider the biotites: 28, 89 and 436. Biotite 28 coexists with a garnet which contains 22.4% FeO but is Mg-poor (5.8%) due to the preferential entry of Mg into the coexisting chlorite. Biotite 89 belongs to the K-feldspar-sillimanite zone and coexists with an almandine-rich garnet (28.4% FeO), but has a low Mg content (5.3% MgO) and a high Fe_2O_3 (25.6%) which must be related to the original bulk composition of the host rock. The same can be said of biotite 436, coexisting with almandine garnet (33.9% FeO) and staurolite and still very Fe-rich (24.1% Fe_2O_3).

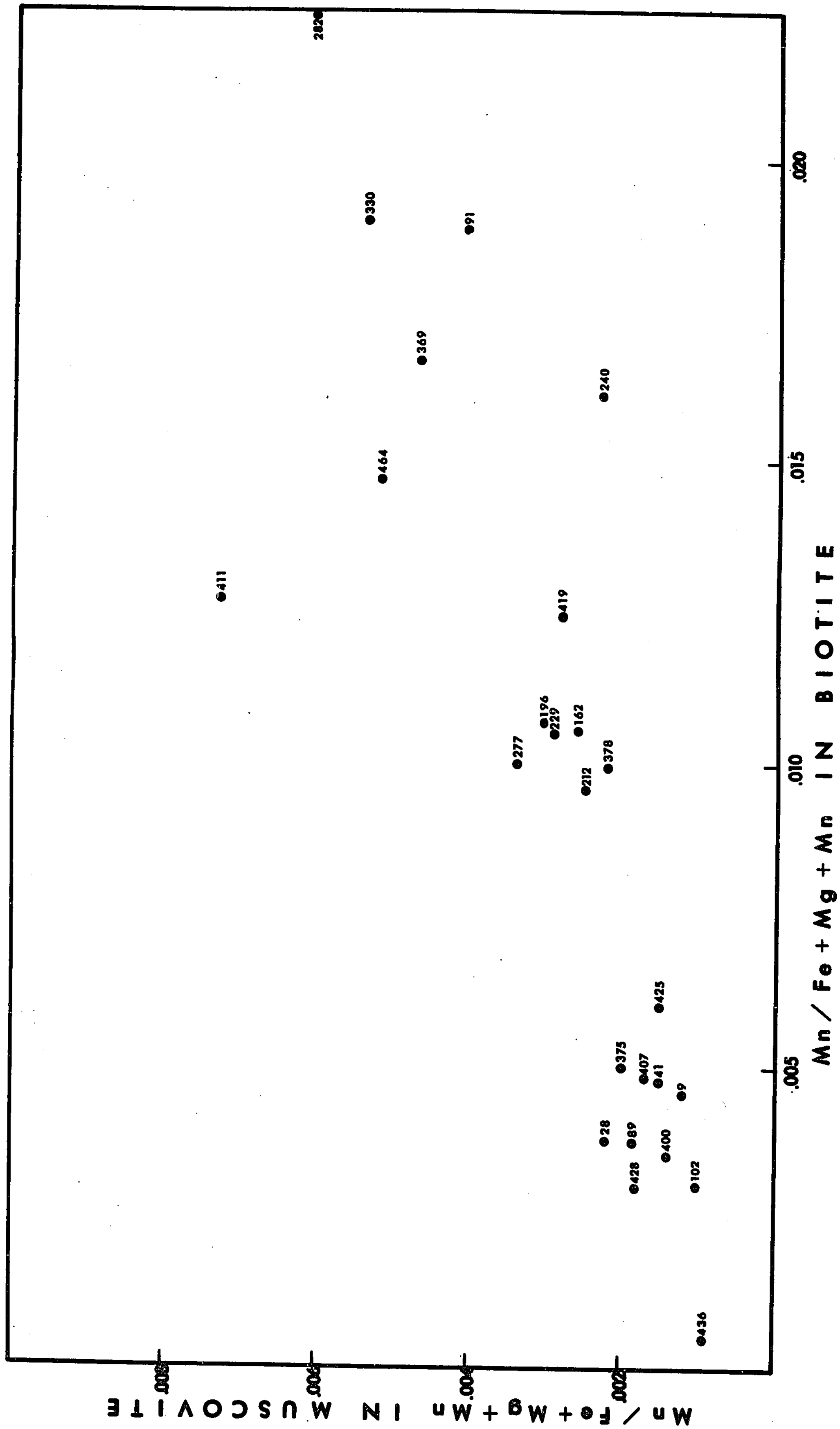
In conclusion, no trend of variation in the amount of Fe and Mg in biotites with metamorphic grade can be recognized due to the different bulk compositions and mineral assemblages.

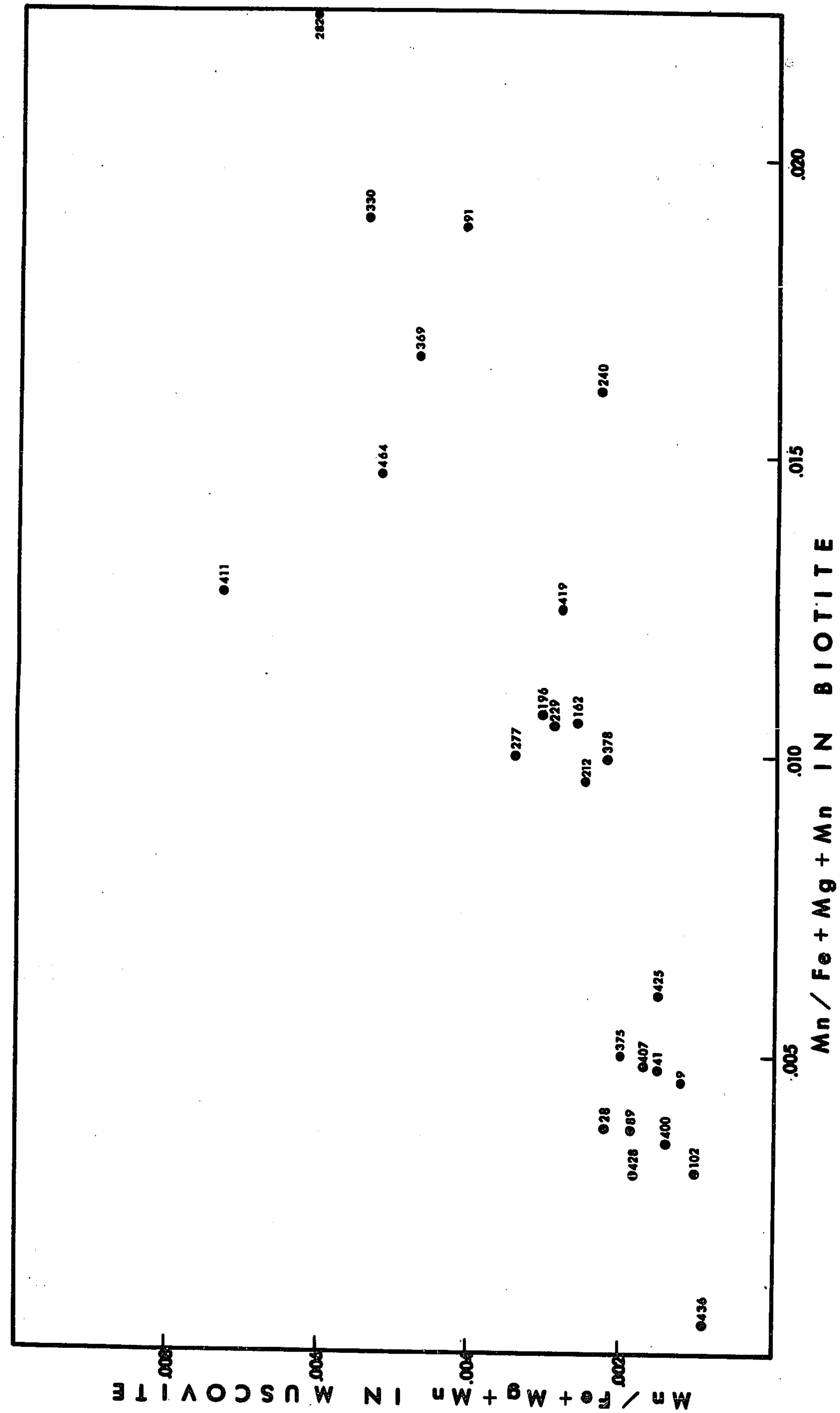
Element distribution between coexisting biotite and muscovite

Distribution of manganese

The distribution of Mn between coexisting muscovite and biotite is shown in fig. 2. The values X_{Mn} are expressed as the ratios of the number of cations of Mn divided by Mn + Mg + Fe (total iron). Some scattering of points exists, but a straight linear trend can be recognized. A more regular distribution might have been obtained by using a different atomic ratio, such as $Mn/Fe^{2+} + Mg + Mn$ (considering only the bivalent cations), or Mn/Fe + Mg + Mn + Ti + Alvi (considering all the major octahedrally bound cations). The scattering of points from a simple straight line is probably partly due to analytical error, for the Mn content of muscovite is extremely small (.OX weight %) and accuracy is difficult to obtain at this level.

Fig.2- Distribution of manganese between coexisting musco-
vite and biotite.


Mn / Fe + Mg + Mn IN BIOTITE
Mn / Fe + Mg + Mn IN MUSCOVITE
.005
.010
.015
.020
.002
.004
.006
.008
282
330
91
369
240
464
411
419
196
229
162
277
378
212
425
375
407
41
9
28
89
400
428
102
436



Mn / Fe + Mg + Mn IN BIOTITE
.005
.010
.015
.020
Mn / Fe + Mg + Mn IN MUSCOVITE
.002
.004
.006
.008

The most striking feature of figure 2 is the tendency of the points to cluster in three different parts of the diagram corresponding to increasing Mn content in the coexisting micas. Only four points do not follow this general trend: 240, 282, 411 and 436.

Let us consider first the cluster n° 3 at the right hand side of the diagram; it includes only four samples with the following mineral association: muscovite, biotite, plagioclase, quartz, (± K-feldspar). Muscovite and biotite, therefore, (no other ferro-magnesian minerals being present) take up all the Mn existing in the rock: they are, in fact, the most Mn-rich micas in the diagram of fig. 2.

The second cluster (n° 2, central part of the diagram) includes seven points having the following paragenesis: muscovite + biotite + plagioclase + epidote + quartz (± K-feldspar ± chlorite, etc.). Samples n° 162, 212, 229 and 378 are particularly rich in epidote. Epidote is a common mineral in regional metamorphism and is generally associated with low to medium grade metamorphic rocks; it can contain a high amount of Mn (piemontite is, in fact, a Mn-bearing epidote occurring in low grade, regionally metamorphosed schists).

Table n° 4 (p.51) gives the chemical composition of analyzed epidotes. They all seem to belong to the epidote-clinozoisite series and the amount of Mn present in generally low. Comparing the Mn-content in biotite, muscovite and epidote, biotite seems to contain more Mn than the coexisting epidote (the trend is reversed only in specimens n° 199 and 229) and muscovite, less.

The presence in the assemblages of cluster n° 2 of another Mn-bearing mineral such as epidote, decreases the amount of the element available to enter the mica structure.

Specimens n° 196, 277 and 419 contain about 1% modal epidote which has not been analyzed. An originally Mn-poor bulk composition can be inferred for these samples.

The third group of points (cluster n° 1) lies in the low Mn side of the diagram. It includes different assemblages:

1) muscovite + biotite + plagioclase + quartz + calcite ± K -feldspar ± sillimanite, etc.) (samples n° 41, 375, 407 and 425). No Mn-bearing minerals occur besides muscovite and biotite.

2) muscovite + biotite + plagioclase + quartz + calcite + chlorite or hornblende (samples n° 9, 102, 400, 428). Here another mineral (chlorite or hornblende) which can contain Mn is present. No chemical data are available on the composition of these minerals but, most probably, the bulk composition is responsible for the Mn content of the micas (as in the previous case n° 1).

3) muscovite + biotite + plagioclase + garnet + quartz ± chlorite ± staurolite ± sillimanite ± K feldspar, etc.

(samples n° 28, 89 and 436). The manganese content of the garnets is respectively: 9.3% (for G.28), 4.1% (for G.89) and 1.1% (for G.436). In this case, the low Mn-content of the coexisting micas must be attributed to the occurrence of another mineral species that has a much higher affinity for Mn (i.e. garnet).

The chemical composition of eight garnets which have been analyzed by atomic absorption is given in table 3. The samples are listed in order of increasing metamorphic grade and the atomic ratios are also shown.

The high Mn-content of epidote, muscovite and biotite in specimen n° 282 is responsible for the position of the sample in the diagram of fig. 2. Sample n° 411 contains a garnet (12.9% MnO) and sample n° 240 has garnet (7.4% MnO), epidote (.37% MnO) and hornblende. The micas are rather rich in Mn, but no explanation is available at the moment to justify the anomalous position of these samples in the diagram. Lack of equilibrium with regard to the distribution of Mn seems the only possibility. In conclusion the total amount of Mn in coexisting muscovite and biotite is controlled by the bulk composition of the host rock and by the different mineral paragenesis and no relationship seems to exist with the variation of grade of metamorphism. In this respect, let us consider samples n° 28 and 89 which belong respectively to the garnet and K-feldspar-sillimanite zone and both contain garnet in the assemblage. Notwithstanding the difference in metamorphic grade, they plot very close to each other in fig. 2.

Distribution of lithium

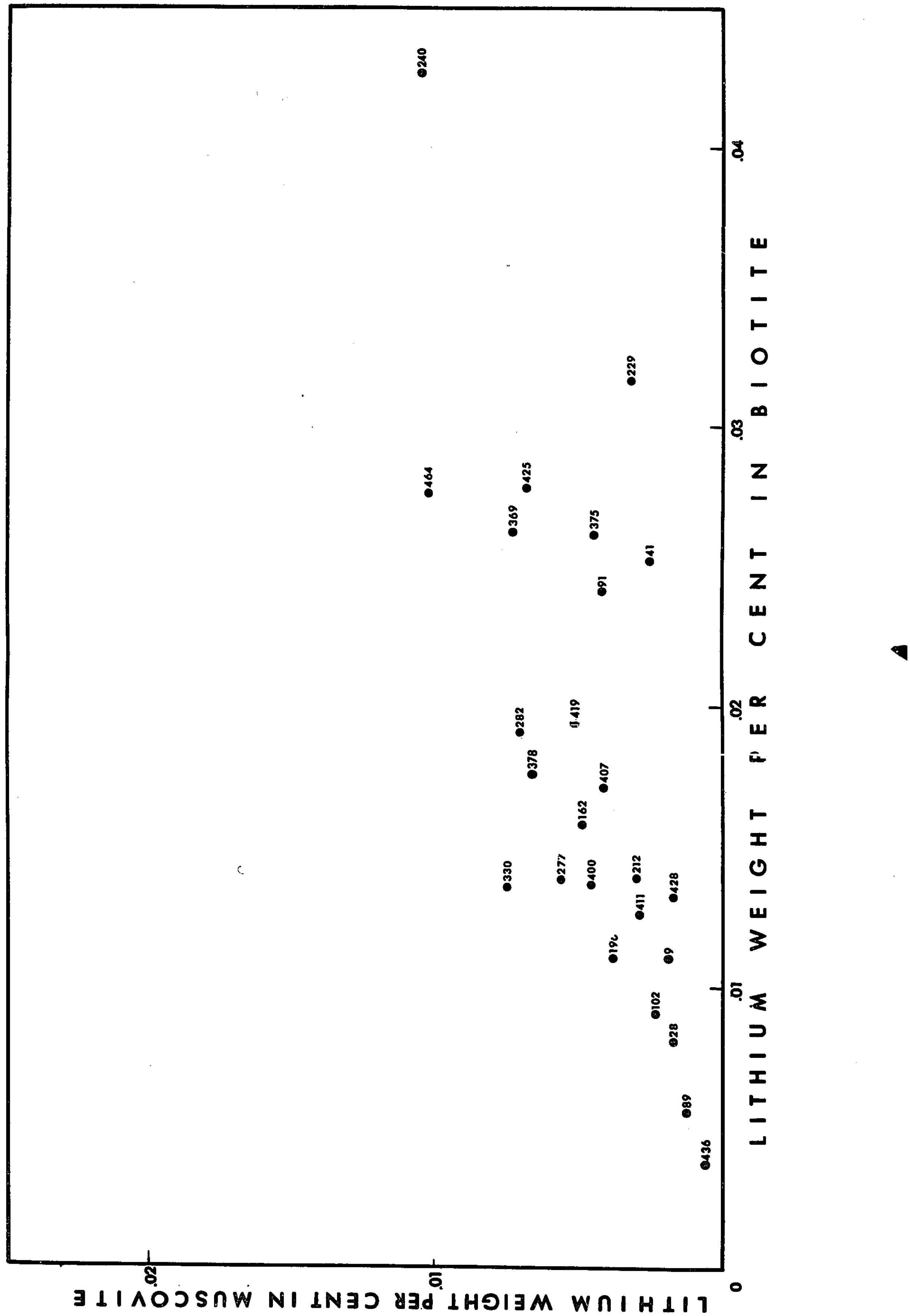
Fig. 3 shows a plot of the weight percent Li in coexisting muscovite and biotite. A straight linear relationship is evident and the scattering is probably due to analytical error.

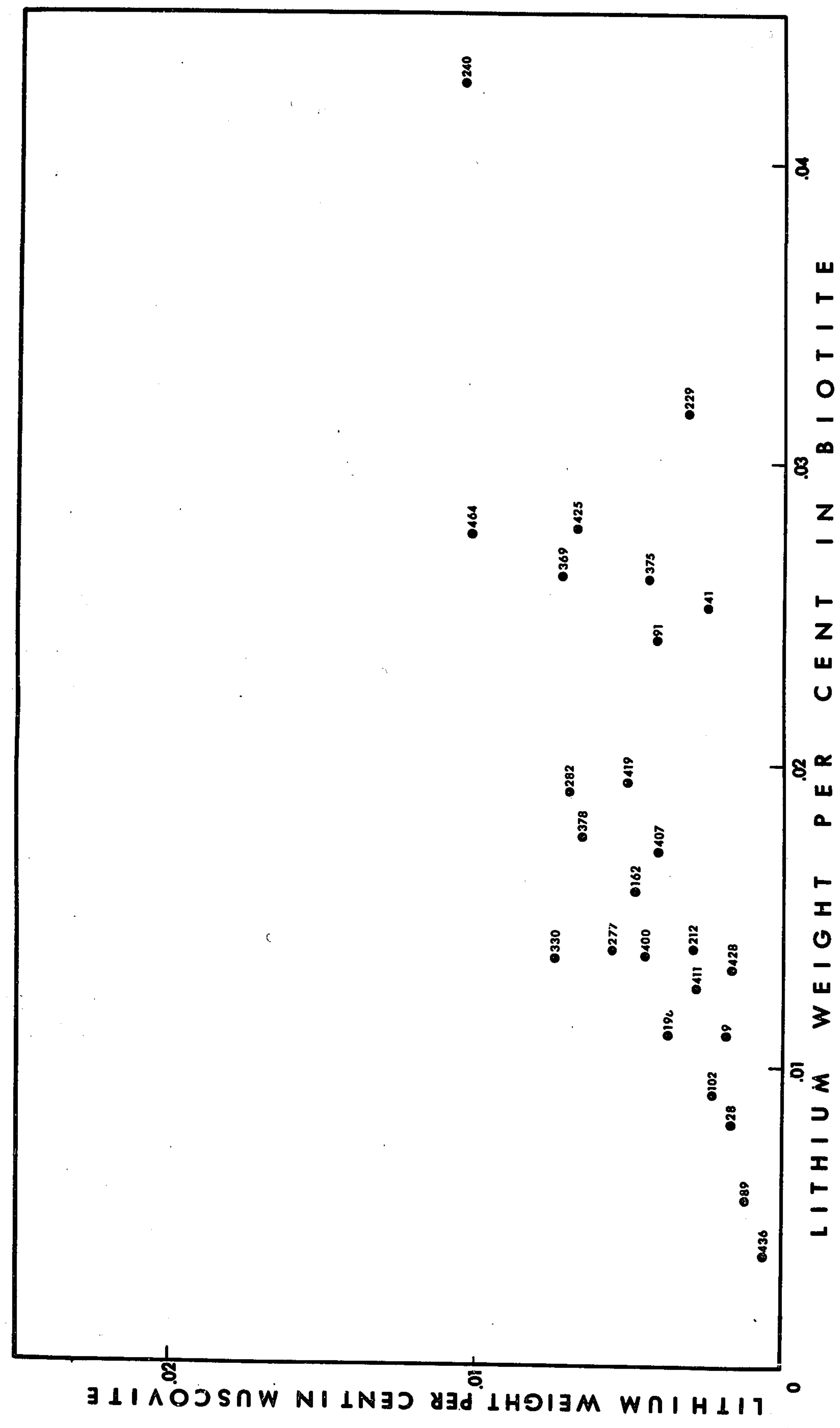
Rankama and Sakama (1950) recognized that with reference to the coordination number, lithium differs totally from the other alkali metals. In lithium micas, the Li^{+} ion does not occupy a structural position similar to that of the K^{+} ion but replaces Al^{3+} and Mg^{2+} in the structure. As a result of its geometric preference for 6-fold coordination, lithium, therefore, tends to accumulate in ferromagnesian silicates.

A comparison of the ionic radii (Å) of some octahedrally coordinated ions follows as given by Ahrens (1952):
Al^{3+} = .51, Fe^{2+} = .74, Fe^{3+} = .64, Mg^{2+} = .66, Mn^{2+} = .80, Li^{1+} = .68, Ti^{4+} = .68 and Cr^{3+} = .63.

Lithium is within ± 15% of the radii of both the major cations (Mg^{2+} and Fe^{2+}) and is, therefore, eligible for camouflage or lattice substitution, but, owing to its lower

Fig.3- Distribution of lithium between coexisting muscovite and biotite.


LITHIUM WEIGHT PER CENT IN BIOTITE
.01
.02
.03
.04
LITHIUM WEIGHT PER CENT IN MUSCOVITE
0
.01
.02


LITHIUM WEIGHT PER CENT IN BIOTITE
LITHIUM WEIGHT PER CENT IN MUSCOVITE
0
.01
.02
.03
.04
.01
.02
240
229
464
425
369
375
41
91
282
419
378
407
162
330
277
400
212
428
411
9
102
28
89
436

charge, the coupled replacement of a trivalent ion would be necessary. Li^{1+} would, therefore, enter suitable structures by admission. Strock (1936) suggested that the replacement of Li^{+1} for an octahedrally bound cation such as Mg or Fe^{2+} is possible only when the electrical balance of the structure is maintained by the introduction of a trivalent 6-coordinated cation according to the equation 2 $Mg^{+2} \rightleftarrows Li^{+1} + R^{+3}$. Foster (1960), in her study of lattice substitutions in micas, states that when Li^{1+} substitutes for Al^{3+} in dioctahedral micas, the charge created in the octahedral layer could be compensated if the ratio Li: (Al replaced by Li) were 3:1 with lithium occupying vacant octahedral sites.

Siroonian et al. (1957) recognize the tendency for lithium to concentrate in micas and hornblende, with lower figures for epidote, feldspar and quartz. This agrees with the view that Li^{1+} is admitted to minerals with octahedral positions. The above-mentioned authors recognize a tendency for biotite to contain a little more lithium than muscovite, but state that this cannot be fully substantiated because of the experimental error in the determination. The diagram of fig. 3 shows without any doubt the higher affinity of the biotite structure for Li and proves the validity of Siroonian's statement.

Distribution of iron and magnesium

The atomic ratio Fe/Fe + Mg in muscovite is shown against the same ratio in biotite in fig. 4. A non-linear plot is obtained as the concentration of Fe is too high to follow the Nernst's distribution law. The scattering of points observed in figure 4 could be reduced by considering the Fe^{2+} and Fe^{3+} distribution as in the following ratios:

$X_{Fe^{2+}} = Fe^{2+}/$ octahedrally bound cations (Fe, Mg, Mn, Al, Ti)

and

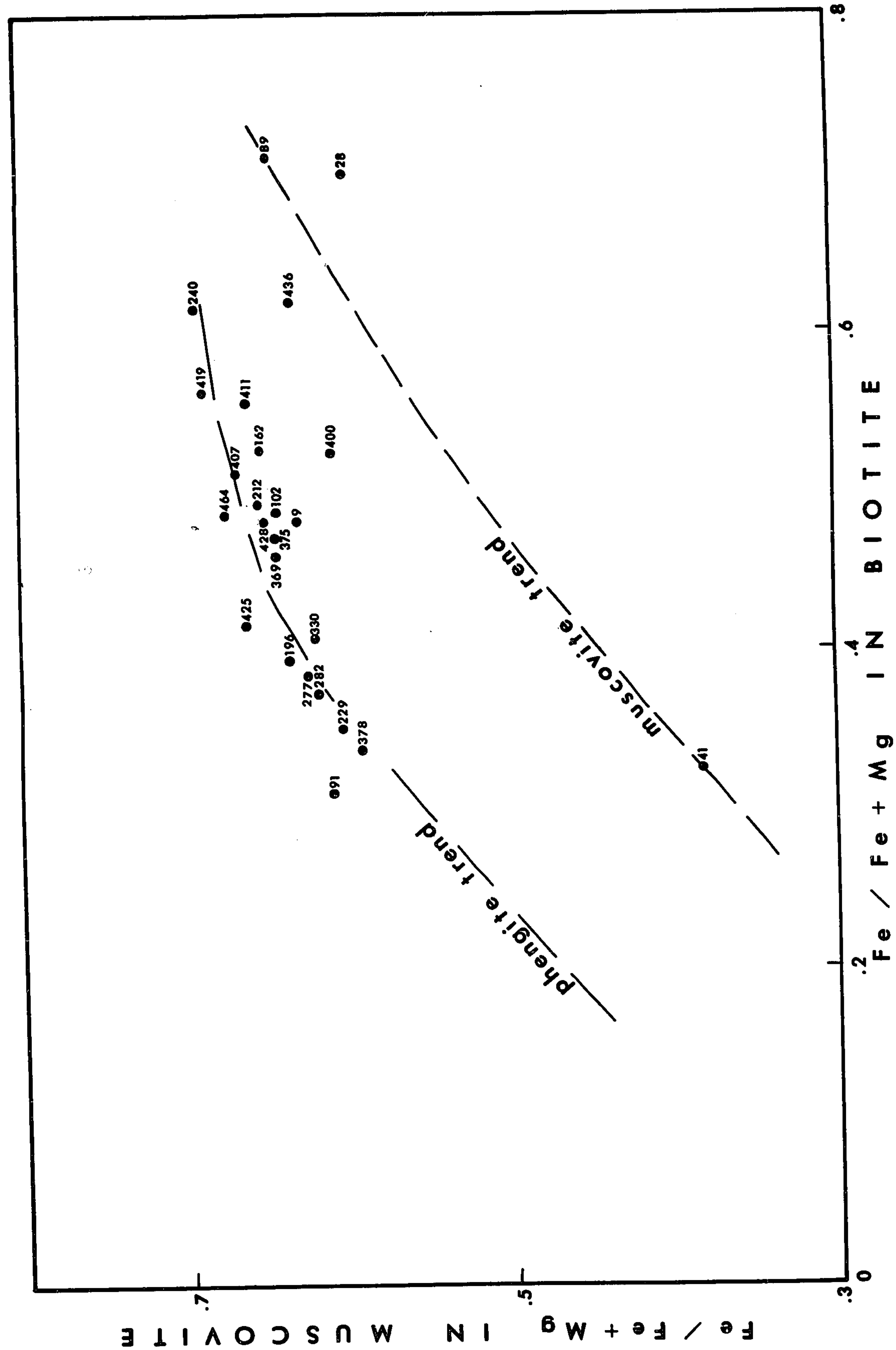
$X_{Fe^{3+}} = Fe^{3+}/$ octahedrally bound cations.

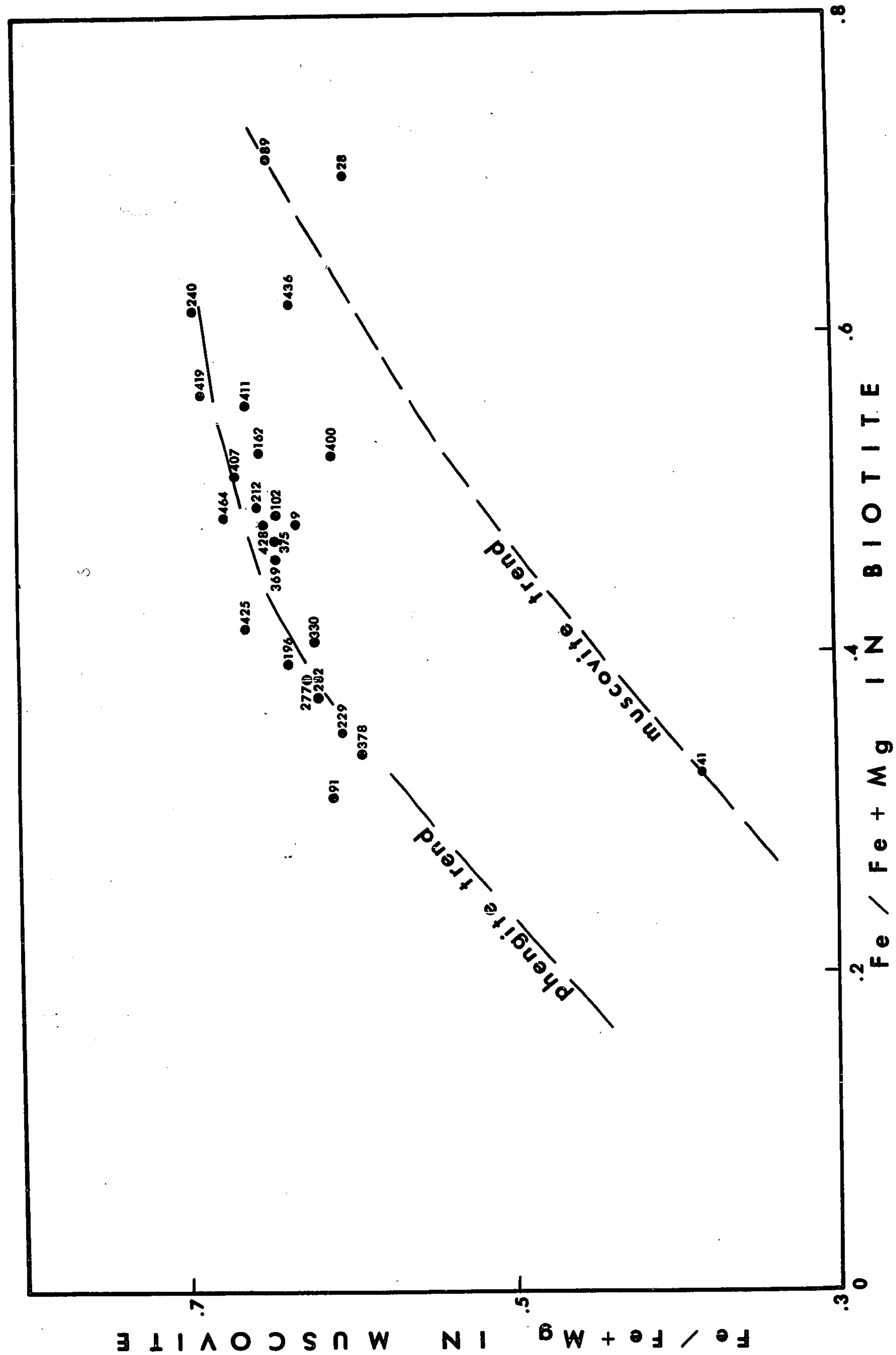
No data on the Fe^{2+}/Fe^{3+} ratios are available and only the total iron distribution can be discussed.

The X_{Fe} ratio for muscovite varies from .6 to .7 and for biotites, from .3 to .7. The biotites having the highest X_{Fe} ratio (411, 240, 436, 28 and 89) coexist with garnet. Two of these five samples (411 and 240) lie on the distribution curve or very close to it but the other three (436, 28 and 89) do not follow this general trend and are characterized by a lower X_{Fe} atomic ratio for muscovite. The muscovites n° 436, 28, 89 and 41 are Fe-poor, Al-rich muscovites (the Al_2O_3 content of muscovite 28 is not available but, in view of the low Fe_2O_3 and MgO content, it is inferred to be high), and seem to define a trend that roughly parallels that shown by the phengites (as in fig. 4). More data relative to Al_2O_3

Fig.4- Distribution of iron between coexisting muscovite and biotite.

Fig.5- Distribution of magnesium between coexisting muscovite and biotite.


Fe / Fe + Mg IN BIOTITE
Fe / Fe + Mg IN MUSCOVITE
muscovite trend
phengite trend
0
.2
.4
.6
.8
.3
.5
.7
89
28
240
436
419
411
162
400
407
464
212
102
9
428
375
369
425
330
196
277
282
229
378
91
41


Fe / Fe + Mg IN BIOTITE
Fe / Fe + Mg IN MUSCOVITE
0
.2
.4
.6
.8
.3
.5
.7
muscovite trend
phengite trend
89
28
240
436
419
411
162
400
407
464
212
102
9
428
375
369
425
330
196
277
282
229
378
91
41

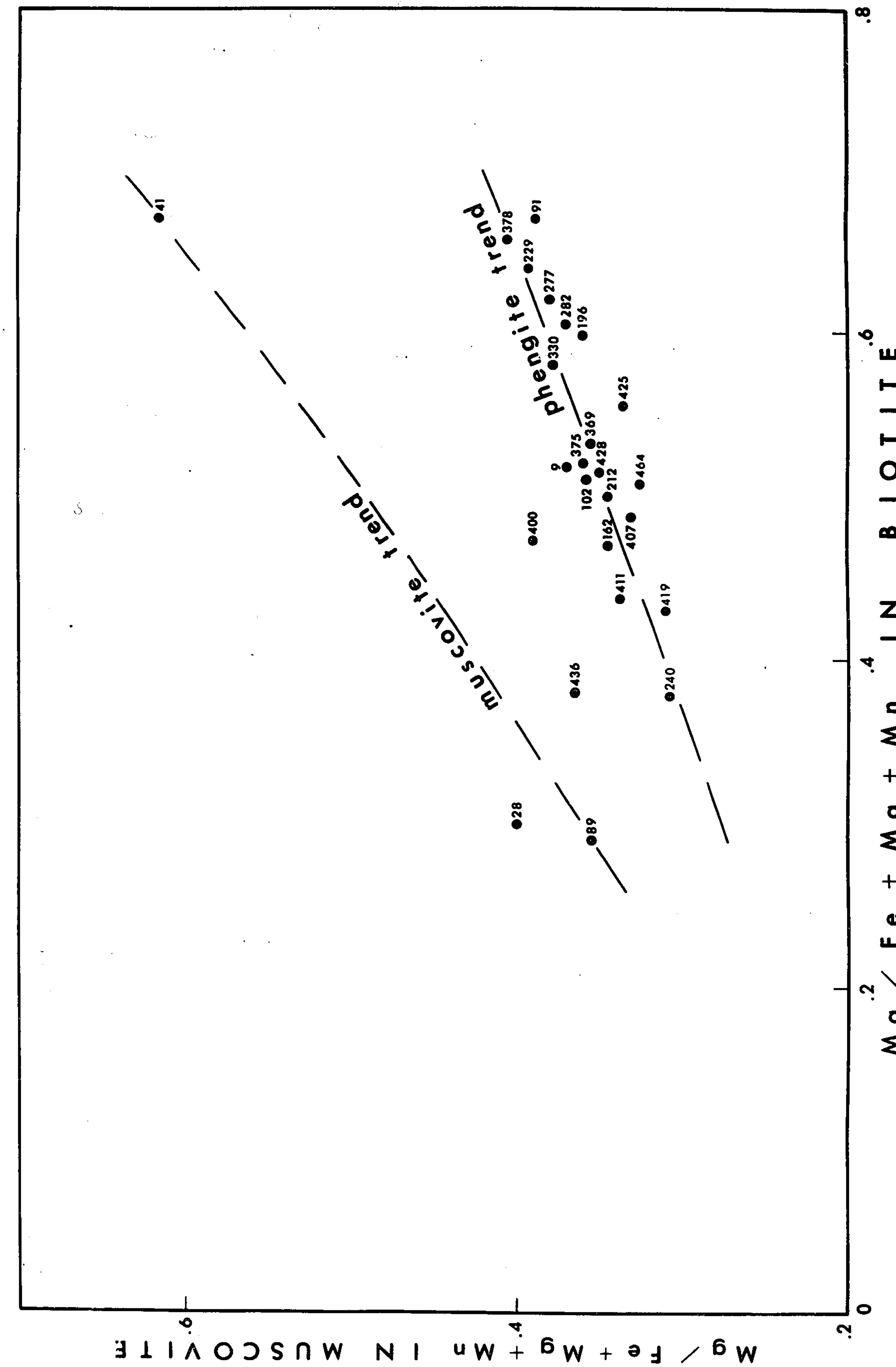
rich muscovites are necessary but, at the moment, it is possible to state that an increase of aluminum in muscovite decreases its affinity for Fe with respect to the coexisting biotite.

The presence of retrograde chlorite after phengite and biotite in sample n° 400 might be responsible for its anomalous position. The trend observed in fig. 4 can be partly related to the increasing metamorphic grade (in fact, sample n° 436 occurs in the sillimanite zone, slightly below the sillimanite-garnet-biotite isograd and samples 41 and 89 belong to the K-feldspar sillimanite zone), but sample n° 28 (which contains also garnet and chlorite) is in the garnet zone and its position must be related to its particular mineral paragenesis and bulk composition.

The distribution of Mg between muscovite and biotite is shown in fig. 5. The ratio used is Mg/Fe + Mg + Mn. The distribution curve is symmetrical with respect to that of fig. 4. The X_{Mg} atomic ratio in phengites is lower than in muscovites and an increase of aluminum in muscovite seems to increase its affinity for Mg.

Distribution of titanium

The crystal chemical role of titanium in micas has been discussed by many authors and different opinions have been expressed. Rankama and Sakama (1950) recognize the possibili-


Mg / Fe + Mg + Mn IN BIOTITE
Mg / Fe + Mg + Mn IN MUSCOVITE
muscovite trend
phengite trend
0
.2
.4
.6
.8
41
378
91
229
277
282
196
330
425
369
375
9
428
212
102
464
400
162
407
411
419
436
240
28
89

ty of the occurrence of Ti in two oxidation states, Ti^{4+} and Ti^{3+}, Ti^{3+} having a radius of .69 and a coordination number of 6, would replace Al^{3+}, Fe^{3+} and Mg^{2+} in octahedral coordination. Schwarz (1967) states that optical spectra suggest that Ti^{3+} is present in biotite. Verhoogen (1962) thinks that in silicates if Fe is present, Ti^{3+} occurs as a product of the following reaction:

$$Ti^{4+} + Fe^{2+} = Ti^{3+} + Fe^{3+}$$

and strongly reducing conditions are not required. Entrance of Ti in octahedral sites requires a replacement of silicon in tetrahedral coordination by 2 or 3-valent ions. The most likely element to substitute for Si is Al^{3+} and the introduction of Ti^{3+} requires less substitution than Ti^{4+}. Verhoogen (1962) concludes that, "whether Ti replaces Si directly in z-sites or whether it replaces in y-sites Al, Mg or Fe which in turn replace Si to restore the charge balance, the result is that silica is removed. Ti-substitution would thus be favoured by low silica activity as well as by high temperatures".

Serdyuchenko (in Saxena, 1966) in a study of the behaviour of Ti in igneous minerals, concludes that at low temperatures and in acid surroundings "Ti in micas is closer to Mg and Al than Si, the isomorphic replacement of Si by Ti increases with rising temperature and increasing alkalinity."

Engel and Engel (1960) state that Ti^{4+} does not occur in tetrahedral coordination substituting for Si^{4+}, but Ti^{3+} replaces Al^{3+} and Fe^{2+} in octahedra. Kretz (1959) believes that Ti occupies the same sites as Fe, Mg and Mn in biotites and Butler (1967) assumes that in muscovite and biotite, Ti occurs in similar sites as Fe^{3+}, but not Mg^{2+} or Fe^{2+}.

Saxena (1966) suggests that Ti occurs in octahedral as well as tetrahedral positions in micas. He believes that at high temperature, Ti^{4+} can enter the tetrahedral site in significant amounts except when excess Al is available. This implies that the Al content (and other elements) of the rocks up to a certain concentration will determine the Ti content of biotite and muscovite. "The increasing of aluminum in tetrahedral coordination in muscovite with the metamorphic grade would decrease the amount of Al available to fill the tetrahedral sites in coexisting biotites, so increasing the affinity of Ti for the tetrahedral coordination. This might explain why Ti in biotite tends to increase with the metamorphic grade".

Kwak (1967, unpublished Ph.D. thesis, McMaster University) found an increase of Ti in biotite with metamorphic grade, corresponding to a decrease of the other octahedrally bound cations, which might be taken as proof of the presence of Ti in 6-coordinated sites; the parallel increase of Si would strongly suggest that Ti does not replace it, although Ti could possibly exist in tetrahedral layer substituting for Al^{3+}.

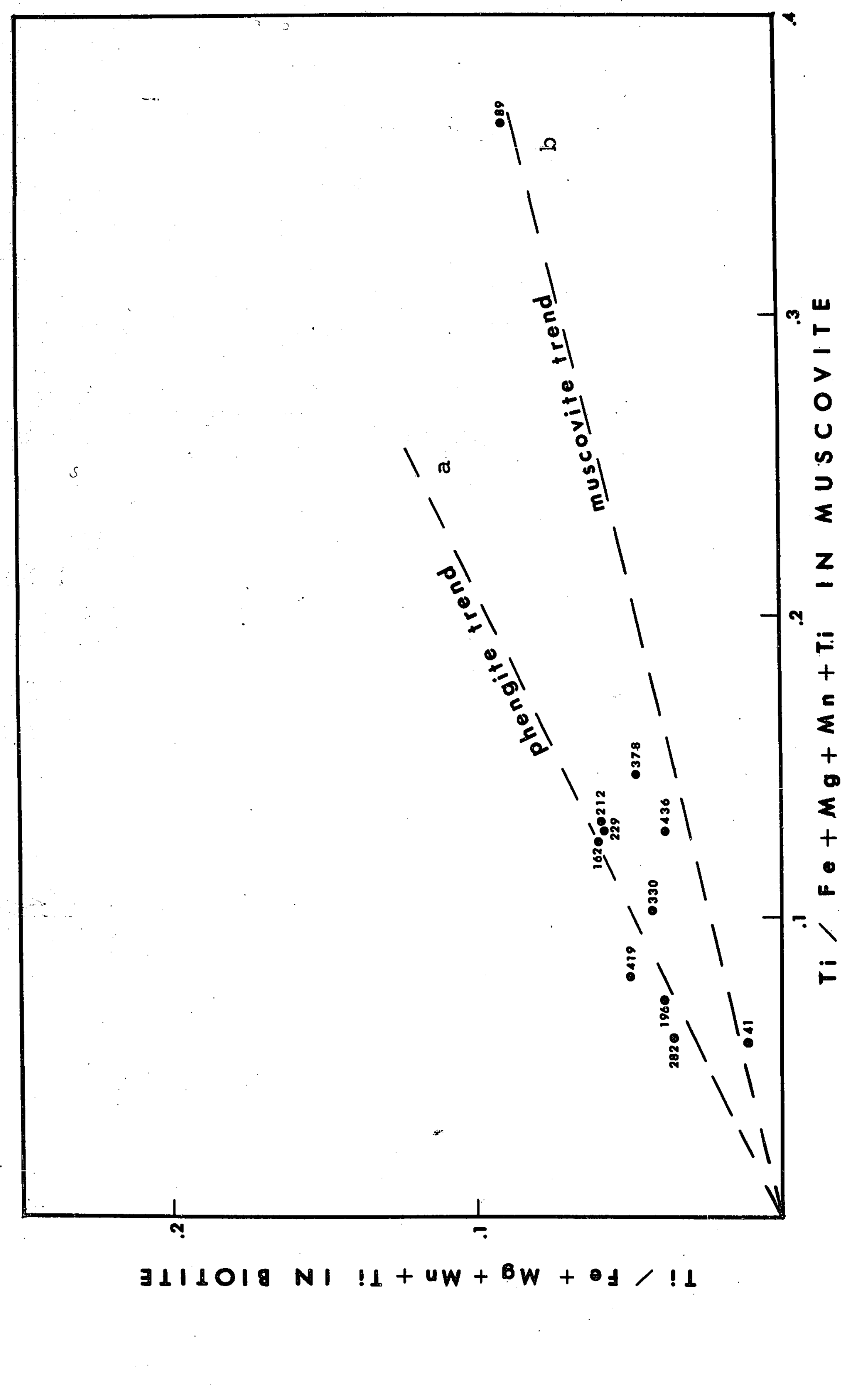
The ratio Ti/Fe + Mg + Mn + Ti in muscovites is presented against the same ratio in biotites in fig. 6. Seven of the eleven samples represented in figure 6 define a straight distribution line (called a), showing that Nernst's distribution law is followed. From the chemical data of tables 1 and 2, it can be observed that biotites always contain more TiO_2 than the coexisting muscovites, but, because of the high amount of iron and magnesium, X_{Ti} in biotites (as previously defined), is lower than the same ratio in the corresponding muscovites. There seems to be a tendency for Ti to concentrate in the more Al-rich mineral of the pair (i.e. muscovite) with respect to the other ions (Fe, Mg and Mn) and this would suggest an affinity of Ti for Al^{3+} in octahedral sites.

If we consider the Al_2O_3 content of the white micas of fig. 6, we can see that the distribution curve a is characteristic of the pair biotite-phengite, while the curve b (defined by the samples n° 41, 436 and 89) is typical of the pair biotite-muscovite.

The anomalous location of 378 could be due to analytical error or disequilibrium or some other compositional variables not known at the moment.

The X_{Ti} ratio in muscovites is higher with respect to

Fig.6- Distribution of titanium between coexisting muscovite and biotite.


.1
.2
.3
.4
Ti / Fe + Mg + Mn + Ti IN MUSCOVITE
.1
.2
Ti / Fe + Mg + Mn + Ti IN BIOTITE
phengite trend
a
muscovite trend
b
89
378
212
229
162
436
330
419
196
282
41

that of biotites than it is for phengites or, viceversa, biotites coexisting with phengites have a higher X_{Ti} ratio than biotites coexisting with muscovites. It is possible to state that an increase of aluminum in muscovite increases its affinity for Ti and decreases the affinity of Ti for the coexisting biotite.

As muscovites are stable over the whole range of metamorphic grade studied, the trend previously defined cannot be correlated with increasing grade.

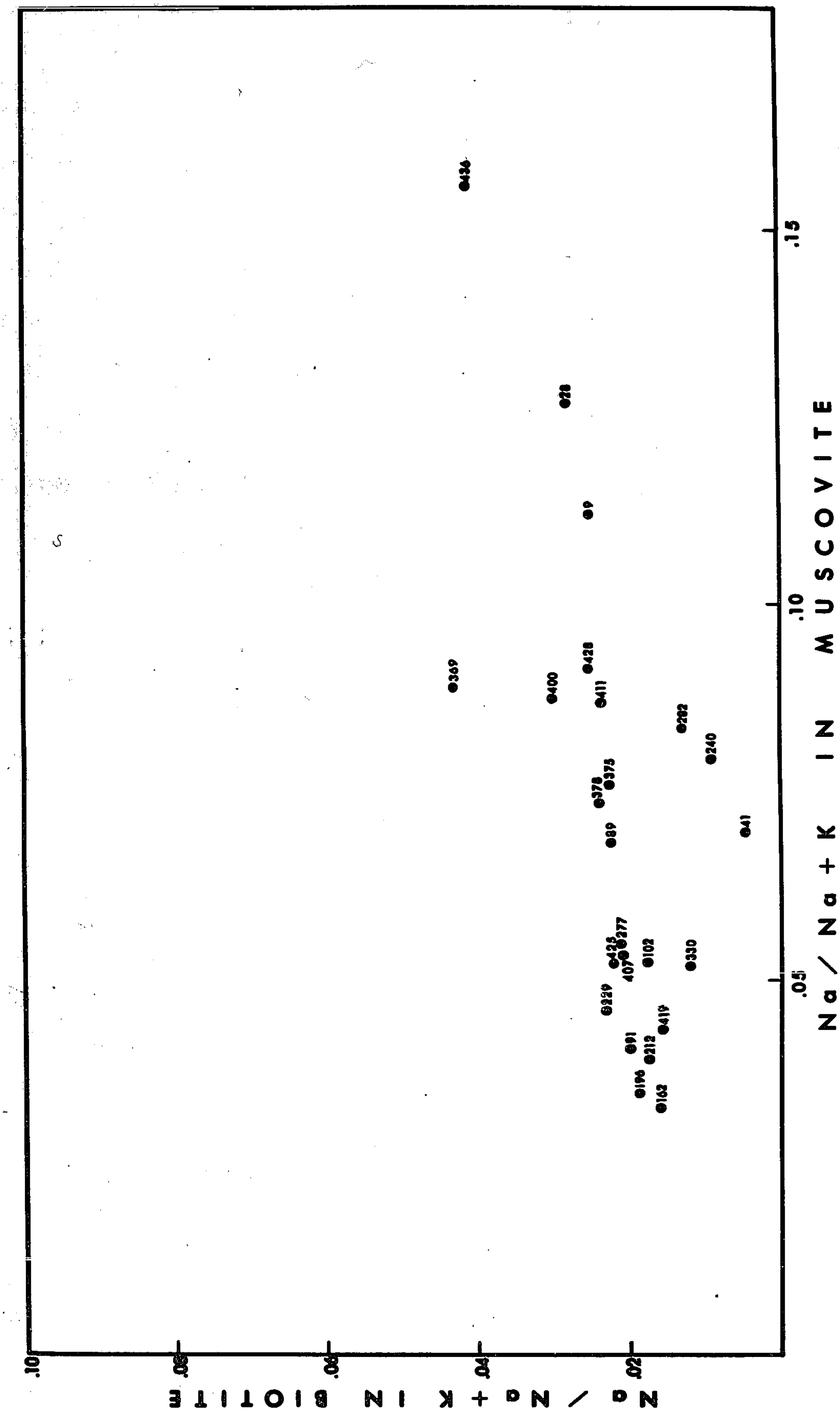
Distribution of sodium, calcium and potassium

The distribution of sodium in the twelve coordinated sites of coexisting muscovites and biotites from the Oak Lake-Whetstone Lake area is shown in figure 7.

Apart from samples n° 369, 330, 41, 240 and 282 (whose biotites have an anomalous Na content), the other points define an almost straight line passing through the origin of the diagram. The Nernst's distribution law is observed and equilibrium with respect to the distribution of Na has been obtained. The metamorphic grade does not seem to affect the partition of Na between muscovite and biotite.

While Na shows a marked preference for the muscovite structure, calcium does not have any well-defined tendency to concentrate in either mineral (even if it seems to pre-

Fig.7- Distribution of sodium between coexisting muscovite and biotite.


Na / Na + K IN MUSCOVITE
.05
.10
.15
Na / Na + K IN BIOTITE
.10
.08
.06
.04
.02
436
28
9
369
400
428
411
282
240
375
378
89
41
277
425
407
102
330
229
419
91
212
196
162

fer to enter muscovite). Saxena (1966) found a relationship between the presence of microcline in the assemblage and the amount of calcium present in biotite and muscovite. He observed that, "samples with more microcline appear to have less Ca in their muscovite and more Ca in their biotite" while in the absence of microcline, muscovite has a lower K and a higher Ca content. No such relationship has been found in the present research.

Conclusions

The distribution of Mn, Li, Fe, Mg, Ti and Na between coexisting micas of the Oak-Lake-Whetstone Lake area suggests that equilibrium has been approached during their recrystallization history. Mn, Li, Ti and Na being present in dilute concentrations are distributed according to Nernst's distribution law.

Some correlations between distribution coefficients and metamorphic grade have been attempted, but generally the wide difference of parageneses and bulk compositions obscures the effects of increasing temperature, and no relationship between the mica composition and metamorphic grade is apparent.

III THE PLAGIOCLASE-EPIDOTE EQUILIBRIUM

Previous Work

Structure and chemistry of the epidote minerals

The structure of the minerals of the epidote group consists of parallel chains of octahedra of composition (Al, Fe^{3+})O_6 and (Al, Fe^{3+})$O_4(OH)_2$, linked edge to edge infinitely along the b crystallographic axis. These chains are bound together by single tetrahedra SiO_4 and double tetrahedral groups Si_2O_7. Outside the chains are located additional Fe^{3+} and Al atoms in octahedral coordination and Ca atoms which occupy large holes between the Si_2O_7 groups and the octahedral chains. The coordination of the Ca atoms is hybrid (7-8). It is then possible to distinguish three different structural positions, all in octahedral coordination, which the Al and Fe^{3+} atoms can enter. Two positions belong to the chains and the third is outside the chains. Because of the smaller size of the cation-anion distances within the chains, the Fe^{3+} atoms are, according to Miyashiro and Seki (1958), accomodated more easily in the positions outside the chains. In this way, if most (Al, Fe^{3+}) sites outside the chains are occupied by Fe^{3+} and most (Al, Fe^{3+}) sites within the chains are occupied by Al, the epidote has a composition near $Ca_2Al_2FeSi_3O_{12}(OH)$ (corresponding to 33% of the Fe^{3+} end member). The structure of an epidote of this composition would be the most stable and unstrained and this would explain the high frequency of epidotes with composition close to this value.

It has been generally accepted in the past that a continuous solid solution existed in the epidote group between pure Al-epidote and common iron epidote (Winchell and Winchell, 1951; Deer, Howie and Zussmann, 1962). In order of increasing Fe amount, four minerals are encountered: α zoisite and β zoisite (both orthorhombic), clinozoisite and epidote (monoclinic). Fe_2O_3 does not completely replace Al_2O_3 and is rarely found in more than 45-50 mole % replacement. The iron content is considered the factor which determines whether the epidote will be monoclinic or orthorhombic.

Coexisting epidotes have been found in natural assemblages by Banno (1964) and Strens (1964-1965), who respectively recognized the existence of a compositional gap in the series zoisite-clinozoisite and clinozoisite-epidote. In particular, Strens (1964) states that, " the stable assemblage clinozoisite (pistacite_{11})-epidote (pistacite_{24}) taken with the scarcity of minerals having compositions in the range 12 to 22% pistacite and the rather dense concentration of analyses of clinozoisite and epidote from low temperature environments around pistacite_{8} and pistacite_{26}

seem to provide strong evidence for a gap in the clinozoisite-epidote series, centered on pistacite$_{17}$ (at about 550° C)".

Strens (1965) explains the cause of the solvus as follows: "The epidote lattice is strained, and hence the free energy of the mixed mineral as a whole is raised when small Al and large Fe ions occupy adjacent sites, but this strain is removed when separation takes place into two components rich in Al and Fe respectively, in which large and small ions are not occupying adjacent sites".

Epidotes and metamorphic grade

Many authors have attempted to relate the epidote composition to the metamorphic grade: Ambrose (1936), Hutton (1940), Sugi (1931), Tilley (1923), Turner (1933) and Vogte (1927) (as referred by Lambert, 1959) found that the lower grade epidotes are iron-rich, the iron content decreasing with increasing grade of metamorphism. But Ambrose and Hutton observe that the very earliest epidotes (in the chlorite zone) are variable in composition from specimen to specimen. Lyons (1955)(in Lambert, 1959) found no relationship between the epidote composition and the metamorphic grade.

Miyashiro and Seki (1958) observed that in the epidotes of the Bessi district, Japan, the lowest grade epidotes fall within the range of about 20-35 molecular % Fe^{3+} end member and with increasing grade of metamorphism, the composition range enlarges up to about 0-50 molecular % Fe^{3+} end member; the enlargement is more pronounced toward the lower Fe^{3+} content than toward the higher; and epidotes with lower contents of Fe^{3+} tend to be more common in higher grades; but the authors stress that the different host rock composition plays a determinant role in defining the amount of Fe^{3+} present in the epidotes so that epidotes in basic schists have a higher Fe^{3+} than in the associated pelitic and psammitic schists.

The plagioclase-epidote equilibrium

The study of the equilibrium between epidote and plagioclase is of great importance in the determination of the boundary between greenschist, epidote amphibolite and almandine amphibolite facies. An increase in the anorthite content of plagioclase with increasing metamorphic grade has been generally recognized. Whereas Na enters mostly the albite molecule of the plagioclase, Ca is a constituent of many metamorphic minerals and, with increasing metamorphic grade, interactions between the An component of plagioclase and the Ca-bearing silicates take place, producing an increase in the An-content.

A corresponding decrease in the amount of the epidote in the rocks parallels the increase of An content of plagioclase with the metamorphic grade. The association albite-epidote has been considered as characteristic of greenschist facies assemblages, the association epidote-plagioclase up to about An_{30} occurs in the epidote amphibolite facies which is marked in its upper boundary by the disappearance of epidote.

Many authors have recognized the occurrence of epidote in a higher grade of metamorphism in association with plagioclase of anorthite content higher than An_{30} and this fact has been mostly attributed to the presence of large amounts of Fe^{3+} in the epidote.

Diadochic substitution between Fe_2O_3 and Al_2O_3 occurs in epidotes but not in plagioclase where the Fe_2O_3 present generally amounts to less than 0.5%. The reverse is true for Na which commonly occurs in very low amounts in epidote. In order to get Na into the epidote structure, it would be necessary for Si to replace Al, as in the case of plagioclases, to balance the valences. Si-Al substitution in tetrahedral coordinated sites is common in plagioclases, but very limited in epidote where most of the Al occurs in 6-fold coordination.

Different equilibria between epidote and plagioclase have been suggested by various authors. Ramberg (1949) considers two possible equilibria occurring in potash-free and potash-rich rocks:

1) $Ca_2Al_3Si_3O_{12}(OH) + 1/2\ Al_2SiO_5 + 1/2\ SiO_2 \overset{T_1}{\rightleftarrows} 2CaAl_2Si_2O_8 + 1/2\ H_2O$

epidote kyanite quartz anorthite

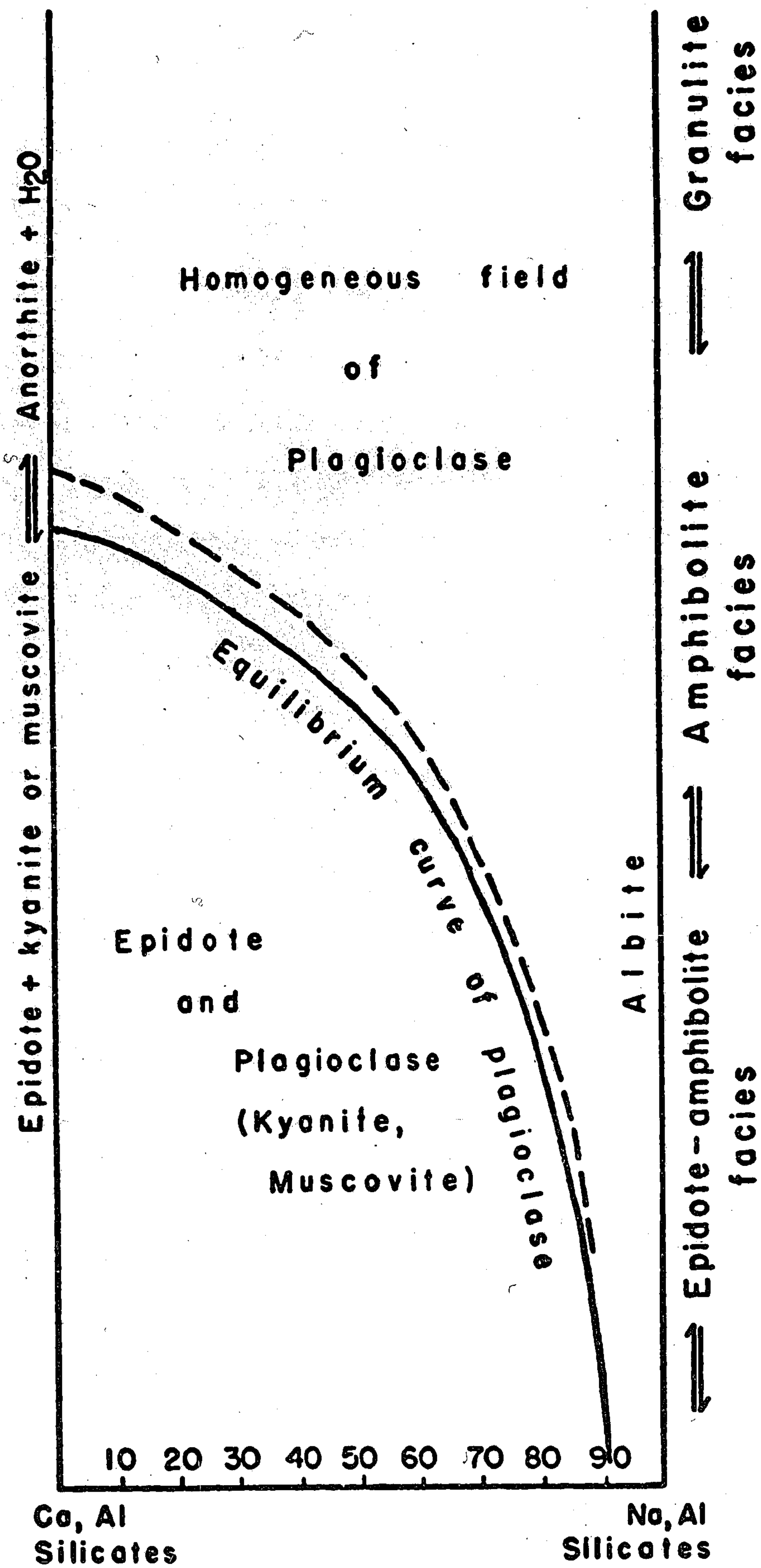
2) $KAl_2Si_3Al\ O_{10}(OH)_2 + 2Ca_2Al_3Si_3O_{12}\ (OH)_2 + 2SiO_2 \overset{T_2}{\rightleftarrows} 4\ CaAl_2Si_2O_8 + KAlSi_3O_8 + 2H_2O.$

muscovite epidote quartz anorthite orthoclase

The equilibration temperature T_2 is higher than T_1. The subsolidus diagrams of the plagioclase-epidote equilibria 1 (solid curve) and 2 (stippled curve) as given by Ramberg are shown in fig. 8. From this diagram it appears that at the same temperature, a plagioclase in K-free assemblages is more Ca-rich than in K-rich assemblages. Ramberg (1949) observes that increasing the H_2O tension and the Fe^{3+}/Al ratio in the rocks displaces the equilibrium toward the epidote side and the curves of fig. 8 will move toward higher temperatures and that in quartz-free rocks, the epidotes may be stable at higher temperatures than in quartzose rocks. He fixes the uppermost stability temperature of epidote at about 470° C.

Ramberg (1952) considers other reactions valid for parageneses rich in calcite:

Fig.8- Subsolidus diagram of the plagioclase-epidote equilibrium (after Ramberg, 1949). The solid and stippled curves represent respectively equilibria 1 and 2 of page 45.


Homogeneous field of Plagioclase
Equilibrium curve of plagioclase
Epidote and Plagioclase (Kyanite, Muscovite)
Anorthite + H_2O
Epidote + kyanite or muscovite
Albite
Granulite facies
Amphibolite facies
Epidote-amphibolite facies
10 20 30 40 50 60 70 80 90
Ca, Al Silicates
Na, Al Silicates

3) $CaAl_2Si_2O_8 + 2\ CaCO_3 + SiO_2 \rightleftarrows Ca_3Al_2Si_3O_{12} + 2\ CO_2$ and
anorthite calcite quartz grossularite

4) $3\ CaAl_2Si_2O_8 + CaCO_3 + H_2O \rightleftarrows 2\ Ca_2Al_3Si_3O_{12}(OH) + CO_2$
anorthite calcite epidote

and admits that the equilibrium temperatures for these reactions are considerably higher than those of equations 1 and 2. Calcite, therefore, stabilizes the association albite-epidote at higher temperature.

The influence of falling temperature on the unmixing of plagioclase in the peristerite compositional field, together with the reaction of plagioclase and epidote has been taken into account by Christie (1959) and Rutland (1961). Christie (p. 270) observes that "below a certain temperature, diffusion of Al and Si ions within the plagioclase would be so slow that the formation of peristerites is negligible, even in geological time. Nevertheless, plagioclase within the exsolution field is unstable, exhibiting higher free energy than do the stable phases (peristerites) and, therefore, possessing higher chemical reactivity. If one of the peristerite members reacts to form new minerals, the exsolution probably would be facilitated".

According to this assumption, epidote in contact with a plagioclase of composition between 5 and 17% anorthite would represent unstable phases. The rarity of this assemblage in nature seems to confirm this statement (de Waard, 1959). The phase diagram of fig. 9b is based upon these considerations.

Compton (1955, 1958) found no break in the frequency of the anorthite content of the plagioclase in amphibolites and greenschists surrounding a trondjemite batholith near Bidwell Bar, California. He suggests that high water pressure raising the epidote-plagioclase reaction curve above the exsolution area of the plagioclase may explain this. A plagioclase in equilibrium with epidote in a contact metamorphic rock will be a high temperature form and will show no break in the frequency of the anorthite content. In this case, the diagram of Ramberg, as given by Christie (1962), is valid (fig. 9a). A systematic variation in the epidote-plagioclase relation may exist between the extreme conditions of contact and regional metamorphism. Study of rocks regionally metamorphosed transitional toward contact metamorphism permits to summarize the difference; going from regional to contact metamorphism (Rutland, 1962),

1) the gap in plagioclase composition is reduced,

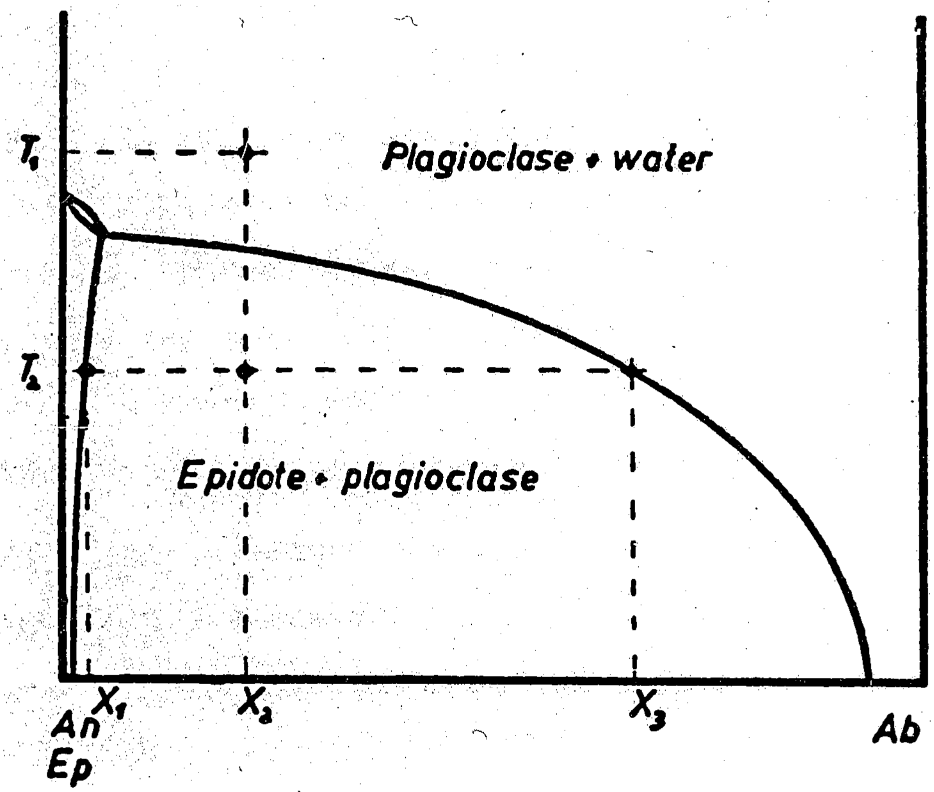
2) Ca enters plagioclase earlier,

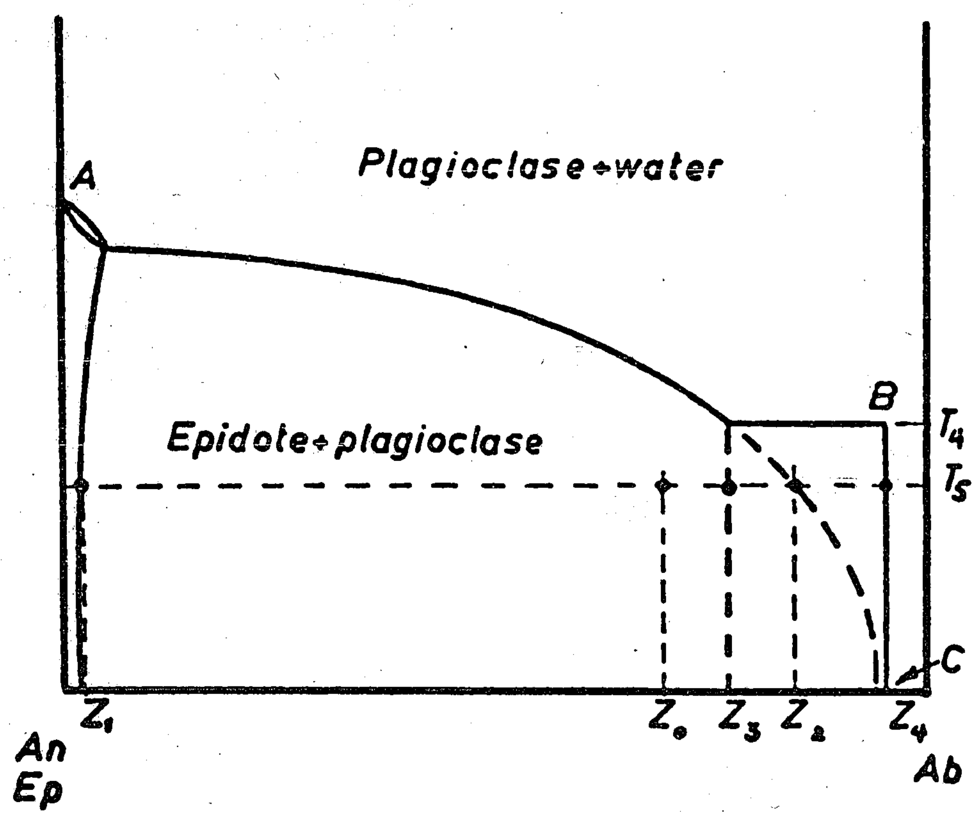
3) epidote tends to disappear earlier.

Mineral Assemblages

Epidote is a common mineral in the Oak Lake-Whetstone

Fig.9- Equilibrium curves for the reaction plagioclase-epidote. 9a : Tentative diagram (Christie, 1962) modified from Ramberg, 1943. This curve is valid when the plagioclase has a quenched high temperature structure. 9b :Equilibrium curve in the temperature range in which peristerites occur. The peristerite exsolution area is between Z_3 and Z_4. According to Christie (1959, p.270) a plagioclase of composition Z_0 would break down at T_5 into epidote Z_1 and a plagioclase Z_2, which is unstable as it lies inside the solvus and it splits into plagioclase Z_4 and Z_3. Plagioclase Z_3 in turn is unstable and breaks down to epidote Z_1 and plagioclase Z_4, which are the final products of the reaction.


Plagioclase + water
Epidote + plagioclase
T_1
T_2
X_1
X_2
X_3
An
Ep
Ab


Plagioclase + water
Epidote + plagioclase
A
B
C
T_4
T_5
Z_1
Z_0
Z_3
Z_2
Z_4
An
Ep
Ab

Lake area. It is always associated with plagioclase and other Ca-bearing minerals such as hornblende, diopside, calcite, garnet, sphene, scapolite and apatite in assemblages ranging from the garnet to the sillimanite-garnet-biotite zone of the almandine amphibolite facies.

The following parageneses have been found:

1) Plagioclase + epidote + biotite + quartz + calcite ($\pm$ muscovite $\pm$ K-feldspar).
2) Plagioclase + epidote + hornblende ($\pm$ quartz $\pm$ diopside $\pm$ K-feldspar $\pm$ chlorite $\pm$ calcite).
3) Plagioclase + epidote + garnet + quartz ($\pm$ hornblende $\pm$ biotite $\pm$ chlorite $\pm$ scapolite $\pm$ calcite).

Sphene, ilmenite, magnetite, apatite, tourmaline are generally present in various amounts.

Chemical Results of Analyses

Table 4 gives the chemical composition of the analyzed epidotes. Some of them are zoned with respect to Fe_2O_3 and Al_2O_3 and the values given in table 4 have been averaged. In brackets are given the lowest and highest Fe_2O_3 values and at the bottom of the table the corresponding amount of pistacite (Ps).

These minerals have a high Ps content and from the chemical and optical data appear to belong to the epidote series.

TABLE 4

Epidote Analyses

sample number	Fe_2O_3	Al_2O_3	TiO_2	MnO	MgO	CaO	Na_2O	K_2O	Ps
15	7.8 (6.5-11.6)	26.2	.16	.01	.01	24.3	.39	.02	17.6 (14.7-26.2)
123	14.5	21.7	.14	.06	.16	24.2	n.d.	.00	32.7
162	13.6	22.2	.11	.27	.06	24.1	.11	.02	30.7
172	8.5	21.1	.12	.13	.20	n.d.*	n.d.	.04	19.2
197	11.3 (10.9-12.4)	25.1	.11	.03	.07	23.7	.11	.04	25.5 (24.6-28.0)
199	11.5 (10.7-14.1)	25.8	.05	.39	.09	23.3	.33	.00	25.9 (24.1-31.8)
212	11.5	24.9	.12	.30	.04	22.6	.23	.03	25.9
229	12.8	22.7	.11	.45	.13	23.9	.12	.02	28.9
240**	13.4	n.d.	n.d.	.37	.20	23.1	.07	.11	30.3
255	10.5	25.0	.07	.11	.04	21.3	.67	.04	23.7
257	9.2 (7.7-11.0)	29.1	.00	.00	.03	24.6	n.d.	.02	20.7 (17.4-24.8)
272	14.5	21.8	.15	.37	.08	23.6	n.d.	.04	32.7
282***	12.6	23.5	.04	.65	.65	23.2	.16	.07	31.6
309	12.5 (11.8-12.8)	23.3	.08	.21	.08	23.8	.22	.01	28.2 (29.1-26.8)
378	12.1	24.5	.05	.06	.05	22.7	.24	.04	27.3
383	12.8 (11.0-14.1)	24.1	.14	.25	.09	22.9	n.d.	.01	28.9 (24.8-31.8)
461	13.5	22.5	.07	.08	.03	23.8	.19	.03	30.5

* not determined

** SrO = .0044

*** SrO = .01

In table 4 all the Fe has been considered as Fe^{3+} and all Mn as Mn^{2+}. The amounts of Mn, alkalies and Mg^{2+} are very low.

No relationship seems to exist between the epidote's composition and the metamorphic grade. The fact that epidotes, when zoned, show an increasing Ps content from the center to the border of the grains, demonstrates their tendency to become progressively enriched in Fe_2O_3 as a result of prograde metamorphism (see Strens, 1965).

Zoning is more marked in low grade assemblages; at higher grade, the epidotes are either homogeneous or less intensely zoned.

In general, however, the great variety of bulk composition and mineral paragenesis obscures any compositional trend. As will be shown later, the reactions by which epidote breaks down to produce the anorthite molecule are greatly dependent on the mineralogy of the samples.

The composition of plagioclases is given in tables 5a and b. The plagioclase grains are generally zoned; normal, reverse and oscillatory zoning have been observed. The average composition and the lower and higher An content are given in the tables together with the kind of zoning.

Table 5b gives the composition of analyzed plagioclases which do not coexist with epidotes. The average An content is lower than in epidote-bearing assemblages. While the

TABLE 5a

Plagioclase Analyses

a] Plagioclases coexisting with epidotes

sample number	Ab	An	Zoning	compositional range (An)	Or
15	65.5	33.5	reverse	26.9-40.0	.90
123	80.6	18.4	oscillatory	13.8-22.5	.95
162	60.1	38.5	normal?	31.5-49.9	1.30
167	68.2	30.8	oscillatory	20.5-40.7	.86
172	77.6	22.3	reverse	19.6-25.6	n.d.
196	64.9	33.8	reverse	28.0-39.7	1.15
199	64.5	34.6	reverse	29.0-39.2	.86
212	73.5	25.6	reverse	22.3-31.2	.86
213	72.6 (nucleus)	26.6	normal	23.5-33.6	.75
	87.4 (rim)	11.8	normal	10.8-13.4	.75
229	58.8	41.8	?	32.4-53.2	.71
255	63.5	35.9	oscillatory	33.2-38.1	.55
257	98.6	1.3	unzoned	-	.10
272	79.2	19.6	normal	12.4-20.8	1.12
282	82.7 (nucleus)	16.3	normal	15.0-17.2	.96
	94.6 (rim)	4.8	normal	3.0- 7.5	.61
309	65.9	33.1	normal	29.6-34.4	1.45
378	76.2	22.2	reverse	17.1-25.8	1.51
382	83.0	16.3	reverse	14.0-18.6	.62
461	73.6	25.4	reverse?	24.0-28.8	1.07

TABLE 5b

Plagioclase Analyses

b] Plagioclases not coexisting with epidote

sample number	Ab	An	Zoning	compositional range (An)	Or
41	91.9	7.2	normal	.7-15.6	.90
89	83.2	17.5	normal	10.8-20.8	.70
192	90.7	8.3	unzoned	-	.90
289	90.8	8.5	normal	.9-12.7	.64
319	98.7	.78	unzoned	-	.52
330	92.8	6.3	normal	4.6- 8.3	.86
419	88.1	11.0	normal?	6.1-16.9	.83
431	91.6	7.7	unzoned	-	.67
436	92.6	6.8	unzoned	-	.47
444	89.5	9.9	oscillatory	4.5-16.9	.55
447	90.8 (nucleus)	8.6	reverse?	6.2-10.0	.48
	97.0 (rim)	2.5	normal	1.0- 4.5	.48
459	92.1 (nucleus)	7.2	normal	5.5- 8.7	.61
	96.8 (rim)	2.5	normal	.9- 3.7	.61
463	92.1 (nucleus)	6.9	oscillatory	6.0- 9.5	.90
	97.5 (rim)	1.5	normal	.7- 3.2	.90

plagioclases of table 5a are mostly oligoclases and andesines, those of table 5b are albitic in composition.

This demonstrates that in epidote-free assemblages, albite is stabilized at higher temperature through all the almandine amphibolite facies , that the breakdown of epidote is responsible for the increasing anorthite content of plagioclase and that the association epidote-plagioclase with composition in the range of peristerites is unstable.* The zoning is well-developed: usually two, three (rarely four) zones occur which are separated by a sharp or gradational boundary.

The kind of zoning expected to take place in plagioclases of metamorphic rocks affected by a prograde metamorphism is the opposite to that shown by igneous plagioclases. The reverse zoning is usually explained as a result of the generally recognized tendency of the anorthite content of plagioclase to increase with the metamorphic grade (Cloos and Hietanen, 1941; Miyashiro, 1958; Rutland et al., 1960; Compton, 1955; Cannon, 1962, 1966; Misch, 1954; Barth, 1956).

Normal and oscillatory zonings are also frequent and are probably related to retrograde metamorphism, metasomatism or other factors which will be discussed in more detail in the next chapter.

As anorthite does not accept into its structure more than about .5 Fe_2O_3, any breakdown reaction of epidote to produce anorthite must be selective, consuming preferentially the Al-component, the epidote becoming progressively enriched in pistacite. If zoning occurs in epidotes as a result of a prograde reaction by which anorthite is produced, an increase in Ps toward the outer portion of the grain would be expected. Epidotes zoned according to this principle have been found associated with reversely zoned plagioclase, but while plagioclase is always more or less intensely zoned, zoning in epidote is less common. In this regard, it is important to observe that homogeneization is likely to occur more easily in epidotes than in plagioclases because in the former minerals, it involves simply an exchange of Fe^{3+} and Al^{3+} in octahedral sites between nucleus and rim and no major structural rearrangements are required, while in the latter, the migration of Na and Ca ions must occur in close association with a redistribution of Si and Al in the tetrahedral framework.

In the following paragraph on the basis of the chemical data available and textural observations, some reactions involving epidote and plagioclase will be suggested.

Discussion of Assemblages

Quartz-free basic metavolcanic rocks

At the staurolite zone of the almandine amphibolite facies, basic metavolcanic rocks with the following paragenesis have been found: plagioclase - epidote - actinolite - hornblende - sphene - ilmenite. Medium-grained plagioclase, highly zoned (the zoning is reverse and the composition varies from a minimum of An_{21} to a maximum value of An_{40} in the external rim) and epidote (with a Ps-content rapidly increasing from 13-14% to 25% toward the border) define a matrix in which large and elongated amphibole crystals are immersed. Light-green or colorless actinolite is rimmed or almost completely replaced by dark-green hornblende which has also nucleated as small crystals in the ground mass. Sphene occurs in fine-grained aggregates which rarely include relic ilmenite and is often associated with epidotes or stretched along the large crystals of amphibole.

The lack of quartz in the assemblage suggests that the reactions producing zoning in plagioclase and epidotes and the transformations actinolite $\rightarrow$ hornblende and ilmenite $\rightarrow$ sphene must not consume or produce SiO_2.

The transformation of actinolite to hornblende must occur according to a reaction of the following kind:

5) actinolite + $Al_2O_3 \rightleftarrows$ hornblende + (Fe, Mg)O + SiO_2 by

which Al_2O_3 is supplied and (Fe, Mg)O and SiO_2 are released and, unless more hornblende nucleates, must enter some other minerals. As hornblende occurs also as small grains in the ground mass, it is possible that the (Fe, Mg)O and SiO_2 produced by reaction 5 react with CaO, Al_2O_3, H_2O and more SiO_2 to form more hornblende.

The reaction would be as follows (as the composition of hornblende is not known, reaction 6 is valid only as an example):

6) $4(Fe, Mg)O + 7\ SiO_2 + Al_2O_3 + H_2O + 2\ CaO \rightleftarrows \underset{\text{hornblende}}{Ca_2(Fe, Mg)_4 AlSi_7AlO_{22}(OH)_2}$

For reactions 5 and 6 to take place, a supply of CaO, Al_2O_3, SiO_2 and H_2O is needed.

The reverse zoning of plagioclase can be taken as proof that anorthite molecules are formed at the expense of the Al-component of the epidote. The breakdown of Al-epidote can occur in different ways according to the mineral paragenesis and the various equilibria existing in the assemblage. Reactions 7 and 8 are two possibilities:

7) $\underset{\text{Al-epidote}}{2\ Ca_2\ Al_3Si_3\ O_{12}(OH)} \rightleftarrows \underset{\text{anorthite}}{3\ Ca\ Al_2Si_2O_8} + CaO + H_2O$

8) $\underset{\text{Al-epidote}}{2\ Ca_2\ Al_3Si_3\ O_{12}(OH)} \rightleftarrows \underset{\text{anorthite}}{2\ Ca\ Al_2Si_2O_8} + 2\ CaO + Al_2O_3 + 2SiO_2 + H_2O$

Reaction 7 is more likely to occur in SiO_2 rich environments where quartz is present and SiO_2 can be easily supplied to any reaction.

Reaction 8 is more likely to occur in our case in which CaO, Al_2O_3, SiO_2 and H_2O are required for the transformation actinolite → hornblende to take place and for the nucleation of new hornblende.

An indirect proof that the breakdown of epidote occurs according to reaction 8 is given by the presence of abundant sphene which sometimes includes relic crystals of ilmenite and suggests that a reaction of the following kind must have occurred:

9) $\underset{\text{ilmenite}}{FeTiO_3} + CaO + SiO_2 \rightleftarrows \underset{\text{sphene}}{CaTiSiO_5} + FeO$

The FeO produced by this reaction can easily enter the amphibole molecule and CaO and SiO_2 could be supplied by reaction 8. The complete reaction would be:

10) actinolite + Al-rich epidote + ilmenite ⇄ hornblende + Fe-rich epidote + anorthite + sphene (+ H_2O).

As a result of this reaction, the plagioclase would develop reverse zoning, the Al-content would sharply decrease in epidote, hornblende would grow after actinolite and nucleate in the matrix and sphene would replace ilmenite.

Quartz-bearing basic metavolcanic rocks

At about the same metamorphic grade, in quartz-bearing assemblages, the following mineral association has been

It is interesting to observe that in reactions 12 and 13, CO_2 and H_2O occur in the opposite sides of the equilibria and that at a certain temperature (all the other compositional variables being held constant) the amount of Fe present in s.s. in epidote will be a function of the CO_2/H_2O ratio in the vapor phase. If a reaction occurs which tends to vary this ratio, equilibria 12 and 13 will be displaced toward the left or the right hand side. If, for instance, H_2O is supplied by some other reactions taking place in the rock (such as reaction 11) or by an external source, the above equilibria would move to the left and Fe-epidote would nucleate. The opposite would happen if the partial pressure of CO_2 increases as a result of decarbonation reactions affecting interlayered carbonatic rocks during prograde metamorphism.

Calc-silicate rocks

In calc-silicate rocks, in the amphibolite facies, the assemblage quartz - calcite - epidote - plagioclase - biotite - sphene - tourmaline - magnetite - ilmenite, apatite (hematite) is common over a wide range of metamorphic conditions. Calcite is very abundant and most likely participates in the equilibrium between plagioclase and epidote according to one of the following reactions:

found: quartz, plagioclase, chlorite, hornblende, epidote, Fe-Ti oxides, (biotite), sphene, calcite, apatite. Large porphyroblasts of hornblende have grown partly including a fine matrix constituted by quartz, zoned plagioclase, very fine epidotes and Fe-Ti oxides. Chlorite is usually associated with calcite and epidote and sometimes in interfingered with hornblende.

The reverse zoning of plagioclase, the low amount of epidote and the textural relationships between chlorite and hornblende suggest that the following reaction (Kretz, 1963) must have been taking place:

11) chlorite + Al-epidote + quartz $\rightleftarrows$ anorthite + hornblende + H_2O

In presence of magnetite and of Fe-rich epidote, an equilibrium involving both phases must exist. Reactions 12 and 13 might possibly take place in magnetite bearing assemblages:

12) $\underset{\text{Fe-epidote}}{2Ca_2Fe_3Si_3O_{12}(OH)} + 4CO_2 \rightleftarrows \underset{\text{calcite}}{4\,CaCO_3} + \underset{\text{magnetite}}{2\,Fe_3O_4} + H_2O + 6\,SiO_2 + 1/2\,O_2$

13) $\underset{\text{Fe-epidote}}{2\,Ca_2Fe_3Si_3O_{12}(OH)} + \underset{\text{ilmenite}}{3\,FeTiO_3} + CO_2 \rightleftarrows \underset{\text{sphene}}{3\,CaTiSiO_5} + \underset{\text{magnetite}}{3\,Fe_3O_4} + \underset{\text{calcite}}{CaCO_3} + H_2O + \underset{\text{quartz}}{3\,SiO_2}$

14) $2\ Ca_2Al_3\ Si_3O_{12}(OH) + CO_2 \rightleftarrows CaCO_3 + 3\ CaAl_2Si_2O_8 + H_2O$ or

Al-epidote calcite anorthite

15) $2\ Ca_2Al_3Si_3O_{12}(OH) + 2\ CO_2 \rightleftarrows 2\ CaAl_2Si_2O_8 + 2\ CaCO_3 +$

Al-epidote anorthite calcite

$H_2O + Al_2O_3 + 2\ SiO_2$

quartz

The frequent presence of vermicular exsolutions of quartz in biotite and inclusions of sphene and hematite suggest that an exchange reaction must have occurred by which the release of Si, Ti and Fe^{3+} has been compensated by the entrance of some other element (most probably the Al_2O_3 supplied by reaction 15).

If abundant ilmenite is present, the reaction:

16) $FeTiO_3 + CaCO_3 + SiO_2 \rightleftarrows CaTiSiO_5 + CO_2 + FeO$ produces

ilmenite calcite sphene

rims of sphene around ilmenite and calcite. Joining reactions 15 and 16, we obtain the following reaction:

17) $2\ Ca_2Al_3Si_3O_{12}(OH) + 2\ FeTiO_3 \rightleftarrows 2\ CaAl_2Si_2O_8 +$

Al-epidote ilmenite anorthite

$2\ CaTiSiO_5 + H_2O + Al_2O_3 + 2\ FeO$

sphene

FeO and Al_2O_3 could enter the biotite molecule or FeO could be partly oxidized to Fe_3O_4 introducing equilibrium 12 or 13 previously discussed. The total reaction taking place in the assemblage is:

18) epidote + ilmenite + $biotite_1$ + $CO_2 \rightleftarrows$ sphene + anorthite + $biotite_2$ + calcite + magnetite + SiO_2 + H_2O.

According to this reaction, Al-epidote is consumed and sphene and anorthite are produced. Biotite occurs in both sides of the equation and acts as a sink, its composition changing according to the other reactions taking place in the assemblage.

Retrograde metamorphism or a change of the CO_2/H_2O ratio in the vapor phase can reverse equilibrium 18.

Sample n° 309 has the assemblage discussed above but the plagioclase is normally zoned from An_{34} to An_{29} (sericitic alterations are frequent in the central part of the grains and thin albitic rims are common). Epidote has an average Ps content of 28% but it is slightly zoned, the Fe-component decreasing from about 29.10% to 26.8% in the outer portion of the grains. Grains of calcite often occur as inclusions in epidote or are "framed" by thin continuous skeletal crystals of epidote which seem to have nucleated preferentially at the boundary between grains of calcite.

The textural relationships and the zonal pattern of plagioclase and epidote show that the trend defined by reaction 18 must have been reversed at a certain stage of the development of sample 309. An increase in the CO_2/H_2O

ratio (such as introduction of H_2O or escape of CO_2) would increase the equilibrium temperature of reaction 18 and at constant temperature would stabilize epidote.

Pelitic rocks containing hydrous minerals such as chlorite and micas are often interlayered with calc-silicate rocks and the general tendency of hydrous minerals to break down to produce an anhydrous mineral + H_2O in prograde reactions could have supplied the H_2O necessary to reverse reaction 18.

Pelitic rocks

In muscovite-bearing assemblages the following reaction has been proposed and discussed by Ramberg (1949) and Kretz (1963):

19) $\underset{\text{Al-epidote}}{2\ Ca_2Al_3Si_3O_{12}(OH)} + \underset{\text{muscovite}}{KAl_2Si_3AlO_{12}(OH)_2} + \underset{\text{quartz}}{2\ SiO_2} \rightleftarrows$

$\underset{\text{anorthite}}{4\ CaAl_2Si_2O_8} + \underset{\text{orthoclase}}{KAlSi_3O_8} + 2\ H_2O$.

This reaction does not take into consideration the fact that muscovite, in the temperature range at which reaction 19 occurs, can be phengitic in composition and that the amount of Ps present in s.s. in epidote is generally high.

If K-feldspar is lacking, other equilibria must take place in muscovite bearing assemblages.

<u>K-feldspar-free assemblages</u>. The assemblage: muscovite, biotite, quartz, plagioclase, epidote, calcite, quartz, magnetite, apatite, tourmaline (sphene, ilmenite) is common in the Oak Lake-Whetstone Lake area. The muscovite is phengitic in composition. The tendency of phengite to approach a muscovite composition with increasing metamorphic grade has been observed by many authors. This reaction needs a supply of Al_2O_3. An exchange reaction between phengite and biotite could be possible:

20) $K\,R^{2+}_{.5}\,R^{3+}_{1.5}\,(OH)_2\,Si_{3.5}\,R^{3+}_{.5}\,O_{10}$ + $K\,R^{3+}_{.5}\,R^{2+}_{2.5}$
phengite Al-rich

$(OH)_2\,Si_{2.5}\,R^{3+}_{1.5}\,O_{10} \rightleftarrows K\,R^{3+}_2\,Si_3\,R^{3+}\,O_{10}\,(OH)_2$ +
biotite muscovite

$K\,R^{2+}_3(OH)_2\,Si_3\,R^{3+}\,O_{10}$.
Al-poor biotite

where R^{3+} in tetrahedral coordination is Al^{3+}. This reaction implies that the Al content of biotite decreases as a result of the phengite → muscovite transformation which is in contrast with the generally recognized tendency of biotite to become Al-rich at higher grade. From the chemical data of tables 1 and 2 (page 8 and 9) it can be observed that the biotites coexisting with muscovite are more Al-rich than the biotites coexisting with phengite. If this trend is real, an external supply of Al_2O_3 is needed.

The presence of Ca-rich plagioclase (reverse zoning may occur) and the occurrence of epidote suggest that a reaction such as 8, 15 or 17 must take place according to which the epidote breaks down producing anorthite and supplies Al_2O_3 to phengite.

The entrance of Al_2O_3 into the phengite structure would release SiO_2 (vermicular inclusions of quartz are common) and (Fe, Mg)O + Fe_2O_3 which could partly exsolve as Fe-oxides (inclusions of magnetite or hematite are often present in phengite) or enter other ferro-magnesian minerals such as biotite. Inclusions of sphene, Fe-oxides and quartz (as vermicules) in biotite could have been produced by the exchange: (Fe, Mg)O + Al_2O_3 (+ Fe_2O_3) being introduced and SiO_2 + TiO_2 (+ Fe_2O_3) being released as quartz, sphene and Fe-oxides.

The frequent association in thin section of phengite-biotite and calcite suggests that epidote must break down according to a reaction such as reaction 15 and that micas do not simply exchange Al_2O_3 with the surrounding environment, but are remobilized and nucleate as large flakes, often transversal to the foliation in association with calcite.

Many authors have considered these micas as retrograde because of their random orientation but, if the above assumption is true, in many cases they are a product of a prograde reaction. In presence of magnetite, equilibrium 12 (or 13 if ilmenite and sphene occur) takes place. The complete reaction is:

21) phengite + epidote + biotite$_1$ (+ ilmenite) + CO_2 $\rightleftarrows$

muscovite + biotite$_2$ + anorthite + magnetite (+ sphene)

+ $CaCO_3$ + SiO_2 + H_2O.

At a certain temperature and all the other variables being held constant, the An content of plagioclase and the Ps content of epidote are a function of the CO_2/H_2O ratio in the vapor phase.

<u>K-feldspar bearing assemblages</u>. In K-feldspar-bearing assemblages, epidote and plagioclase probably are related by equilibrium 19.

The common assemblage: quartz - plagioclase - phengite - biotite - epidote - microcline - sphene - ilmenite - magnetite - apatite - (hematite-tourmaline) will be discussed in detail.

Van der Plas (1959) suggests a reaction by which phengite breaks down at higher metamorphic grade producing K-feldspar, muscovite and biotite:

22) $6\ K\ R_{1.5}^{3+}\ R_{0.5}^{2+}\ Si_{3.5}\ R_{0.5}^{3+}\ O_{10}\ (OH)_2 = 3\ K\ R^{3+}_2$

phengite

$Si_3 R^{3+} O_{10} (OH)_2 + K R^{2+}_3 Si_3 R^{3+} O_{10} + (OH)_2 +$

muscovite biotite

$2 K R^{3+} Si_3 O_8 + 3 SiO_2 + 2 H_2O$.

microcline

The SiO_2 released by this reaction could be responsible for the vermicular inclusions of quartz so frequent in micas.

Reactions 19 and 22 can be joined in the following way:

19) 6 epidote + 3 muscovite + 6 quartz $\rightleftarrows$ 12 anorthite + 3 microcline + 6 H_2O.

22) 6 phengite $\rightleftarrows$ 3 muscovite + 1 biotite + 2 microcline + 3 quartz + 2 H_2O.

23) 6 epidote + 6 phengite + 3 quartz $\rightleftarrows$ 12 anorthite + 5 microcline + 1 biotite + 8 H_2O.

According to reaction 23, epidote and phengite react with quartz to produce anorthite, microcline and biotite. The common interfingering between phengite and biotite could be explained in this way.

This reaction does not take into account the Fe-component of the epidote which must increase by subtraction of the Al-component and, if magnetite, calcite, sphene and ilmenite are present, must participate in the equilibria 12 and 13 previously discussed.

The complete reaction is, therefore:

24) epidote + phengite + ilmenite + quartz + $CO_2 \rightleftarrows$ anorthite + microcline + biotite + sphene + magnetite + calcite + H_2O.

Garnet-bearing assemblages

The equilibrium clinozoisite + quartz $\rightleftarrows$ anorthite + grossularite + H_2O has been discussed by many authors (Kretz, 1963; Strens, 1965; Holdaway, 1966).

Holdaway (1966) has been able to reverse this equilibrium in his experiments and has considered a coupled reaction whose components are:

25) $\underset{\text{clinozoisite}}{4\ Ca_2Al_3Si_3O_{12}(OH)} + SiO_2 \rightleftarrows \underset{\text{anorthite}}{5\ CaAl_2Si_2O_8} + \underset{\text{grossularite}}{Ca_3Al_2Si_3O_{12}} + 2\ H_2O$ and

26) $\underset{\text{Fe-epidote}}{2\ Ca_2Fe_3Si_3O_{12}(OH)} + \underset{\text{grossularite}}{3\ Ca_3Al_2Si_3O_{12}} \rightleftarrows \underset{\text{clinozoisite}}{2\ Ca_2Al_3Si_3O_{12}(OH)} + \underset{\text{andradite}}{3\ Ca_3Fe_2Si_3O_{12}}$

Strens (1965) has given a comprehensive account on the equilibria in systems with excess quartz and water and in systems deficient in quartz. He considered the following reactions:

27) 4 zoisite + quartz $\rightleftarrows$ 5 anorthite + grossularite + 2 H_2O

and

28) 6 zoisite $\rightleftarrows$ 6 anorthite + 2 grossularite + corundum + 3 H_2O

and experimentally determined the breakdown temperatures of seven epidotes ranging in composition from pistacite 5 to 31 and found that for each 1% pistacite present, the univariant curve of reaction 27 had been raised by about 3° C. Strens recognizes that epidotes break down by a reaction of the type:

29) epidote + quartz $\rightleftarrows$ Fe-epidote + garnet + anorthite + H_2O

As a consequence of this reaction, the epidote would become progressively enriched in the Fe^{3+} component up to a certain value, after which Fe^{3+} substitutes into garnet until this is saturated and then appears as hematite. At this stage, quartz appears among the products of reaction 29. The stability field of epidote is enlarged by an increase in water pressure and Fe^{3+}/Al ratio and reduced in favour of plagioclase and garnet by addition of albite or reduction of Fe^{3+} to Fe^{2+}.

In the present research, three samples having the paragenesis: quartz - plagioclase - epidote - garnet have been studied in detail. Sample n° 257 contains quartz - albite

(1.30% An) - epidote - chlorite - garnet - hematite. The rock has been subjected to retrograde metamorphism resulting in chloritization of garnet and growth of secondary chlorite and epidote after the pre-existing minerals. The assemblage albite - epidote shows that the temperature condition at which anorthite is produced by the breakdown of epidote has not been reached and that this sample must belong to the greenschist facies.

Garnets 197 and 199 which coexist with quartz, plagioclase and epidote at higher metamorphic grade (sillimanite zone) contain respectively 6.78 and 6.98% CaO, while garnet 257 has about half as much CaO (3.91%). This observation substantiates the assumption that in the presence of epidote, the CaO content of garnet increases at higher grades as a consequence of reaction 25.

Sample 197 has the following assemblage: quartz - epidote - biotite - garnet - scapolite - plagioclase - calcite - hornblende - sphene - ilmenite - tourmaline and apatite.

Large, clear crystals of scapolite have replaced plagioclase and few relic feldspars are preserved as inclusions into the garnet porphyroblasts. Here plagioclases and epidotes are usually associated.

The Fe^{2+}/Fe^{3+} ratio in garnet has not been determined and the andradite content is not known.

Sphene occurs as large subhedral crystals in the matrix but it is often associated with garnet. The presence of abundant ilmenite and calcite and the association garnet - sphene suggest the following reaction:

30) $2\ Ca_2Al_3Si_3O_{12}(OH) + 9\ FeTiO_3 + 5\ CaCO_3 + 12\ SiO_2 \rightleftarrows$
Al-epidote ilmenite calcite quartz

$3\ Fe_3Al_2Si_3O_{12} + 9\ CaTiSiO_5 + 5\ CO_2 + H_2O$ by which
almandine sphene

almandine garnet and sphene are produced.

By association of reactions 25 and 30, we obtain:

31) $6\ Ca_2Al_3Si_3O_{12}(OH) + 9\ FeTiO_3 + 5\ CaCO_3 + 13\ SiO_2 \rightleftarrows$
Al-epidote ilmenite calcite quartz

$3\ Fe_3Al_2Si_3O_{12} + Ca_3Al_2Si_3O_{12} + 9\ CaTiSiO_5 + 5\ CaAl_2Si_2O_8$
almandine grossularite sphene anorthite

$+ 5\ CO_2 + 3\ H_2O.$

As a result of reaction 31, in the presence of ilmenite, quartz and calcite, Al-epidote breaks down, producing an almandine-grossularite garnet in the ratio 3:1 + sphene + anorthite.

Reaction 31 is more realistic than reaction 25 because in regionally metamorphosed pelitic rocks garnets are never rich in grossularite while the almandine component predominates.

It is interesting to observe that the FeO/CaO ratio in garnets 197 and 199 is about 2.9, and, therefore, very close to the value obtained in reaction 31. Scapolite has the following composition: CaO = 17%, Na_2O = 3%, K_2O = .3%. The epidote is zoned, the Fe-content decreasing toward the border from about 28.0% Ps to 24.6%. This result is in disagreement with the trend normally observed in epidotes.

The enrichment in the clinozoisite component can be due to a secondary phenomenon related to the transformation plagioclase $\rightleftarrows$ scapolite. The great abundance of scapolite and tourmaline shows that the very close granitic intrusions have supplied volatiles such as B, Cl, F, SO_4^{--}, H_2O, etc. A reaction producing scapolite and clinozoisite from anorthite has been written as follows:

$$32)\quad \underset{\text{anorthite}}{12\ CaAl_2Si_2O_8} + \underset{\text{calcite}}{4\ CaCO_3} + H_2O \rightleftarrows \underset{\text{scapolite}}{3\ (3\ CaAl_2Si_2O_8 \cdot CaCO_3)} +$$

$$\underset{\text{Al-epidote}}{2\ Ca_2Al_3Si_3O_{12}(OH)} + CO_2.$$

Scapolite does not occur in sample 199 where plagioclase shows reverse zoning from An_{29} to An_{39}. The epidote is zoned in the normal way, the Ps content increasing from 24.00% to about 32% in the rim. The sample has the following paragenesis: quartz - plagioclase - hornblende - biotite - garnet - epidote - ilmenite - sphene - calcite - apatite - pyrite. A complex reaction must take place involving the production of anorthite, sphene, garnet, from ilmenite, epidote and calcite with hornblende and biotite participating in the reaction.

In reducing environments, the Fe^{3+} of epidote could be reduced to Fe^{2+} and produce pyrite, almandine or enter the hornblende or biotite lattice. A complex redistribution of total Fe and Mg must occur between ferromagnesian silicates, oxides and sulphides and only a preliminary account can be given here. The total reaction is possibly:

33) epidote + ilmenite + calcite + quartz (+ biotite + hornblende) + S^{--} $\rightleftarrows$ garnet + sphene + anorthite (+ biotite + hornblende) + CO_2 + H_2O + FeS_2.

Conclusions

Textural and chemical evidence has shown that in plagioclase and epidote-bearing assemblages, anorthite molecules are produced during prograde metamorphism by the breakdown of the Al-epidote component of the epidote minerals. Various reactions have been suggested which are highly dependent on the paragenesis of the host rock. According to these reactions, the plagioclase increases in anorthite (reverse zoning is frequent) while the Al-component of the epidote decreases in amount (zoning may occur by which the pistacite content increases from the core toward the rim of the grains). The CO_2/H_2O ratio in the vapor phase and other compositional variables such as Fe^{2+}/Fe^{3+} in the minerals

IV NORMAL AND OSCILLATORY ZONING IN PLAGIOCLASE

Introduction

The presence of normal zoning in the metamorphic plagioclase of the Oak Lake-Whetstone Lake area can be produced by the following factors:

1) Prograde reactions
   a) consuming anorthite
   b) producing albite as a result of the breakdown of an Na-bearing mineral.
2) Retrograde reactions
   a) reversal of a prograde An-producing reaction
   b) exsolution from alkali feldspars
3) Alkali metasomatism

Normal Zoning

In assemblages containing paragonite, albite could be produced by the breakdown of this mica according to the reaction:

1) $\underset{\text{paragonite}}{NaAl_2(OH)_2\ Si_3\ Al\ O_{10}} + \underset{\text{quartz}}{SiO_2} \rightleftarrows \underset{\text{albite}}{NaAlSi_3O_8} + \underset{\text{aluminosilicate}}{Al_2SiO_5} + H_2O$

Paragonite as a mineral species has not been found in the area studied. From the work of Eugster and Yoder (1955), it appears that the amount of paragonite which will enter participating in the above equilibria seem to be important.

In epidote-free assemblages, the plagioclase is typically albitic in composition which indicates that, in absence of epidote, albite is stable over the whole range of metamorphic grades studied. The lack of assemblages containing epidote + plagioclase (in the peristerite compositional range) proves the instability of such association.

muscovite in solid solution is lower in assemblages in which paragonite is absent and that Na-bearing muscovite breaks down before pure muscovite. According to this statement, some albite can be produced by the breakdown of an Na-rich muscovite.

It is possible (Evans and Guidotti, 1966) that as the temperature increases, muscovite releases Na and becomes progressively enriched in K. The albite produced in this way could be responsible for the thin sodic rims frequently found around more calcic plagioclases.

A prograde reaction consuming anorthite is possible but no evidence of such reaction exists in the assemblages studied; if epidote is present, the textural relationships suggest that epidote is the lower temperature phase and that anorthite is the product of a prograde reaction. Let us consider for instance sample 272 which has the following assemblage: quartz - plagioclase - microcline - biotite - epidote - ilmenite - sphene - magnetite - apatite - tourmaline.

Plagioclase is normally zoned from $An_{20.8}$ to $An_{12.4}$. The grains are usually large, have a homogeneous nucleus, often sericitized, and the composition suddenly drops down to the lower anorthite values at the border which is free from inclusions and alterations.

The following reaction has been suggested by the texture of the sample:

2) epidote + ilmenite + quartz + $CO_2 \rightleftarrows$ anorthite + sphene + calcite + magnetite + H_2O.

This reaction is probably responsible for the higher Ca content found in the core of these feldspars. The normal zoning could be produced by a reversing of the above equilibria due to retrograde metamorphism, to a change in the CO_2/H_2O ratio at constant temperature or to exsolution of albite from K-feldspar.

It is important to keep in mind that all the samples which display a well-defined normal zoning in plagioclase contain K-feldspar in various amounts.

Misch (1954), considering the various factors responsible for normal zoning in feldspars, distinguishes three possibilities:

growth zoning	1) thermal control: in the presence of other lime-bearing minerals, the ability of plagioclase to incorporate anorthite changes with temperature. 2) introduction of Na.
passive zoning	3) replacement of plagioclase by a) Ca-rich minerals or b) K-feldspar.

Cannon (1966) in a study of zoning and twinning of plagioclase of amphibolites and granulites in the Bartica Assemblage, British Guiana, found that normal zoning is most common and distinguishes between continuous and discontinuous normal zoning. The continuous normal zoning is defined by a gradual increase in Na-content, while in the discontinuous, the core and the Na-rich rim are separated by a sharp boundary. He concludes (p. 532) that, "the waning period of metamorphism and later introduction of Na during the metasomatic phase would both contribute to the change in the matrix plagioclase toward a more albitic composition".

In the normally zoned plagioclases studied, continuous zoning is less common than discontinuous. Between a more calcic core and an Na-rich rim, there is either a sharp boundary or a thin, irregular area of intermediate composition. If plagioclase does not coexist with epidote, the core is generally albitic (6-10% An) or, rarely, sodic-oligoclase, and the rim contains about 0-3% An; the compositional difference in this case is not great while in epidote-bearing assemblages, the gap is greater. In sample 282, for instance, which contains epidote, the core has an average composition of 16.4% An and the rim, 4.8%.

The core can be homogeneous or zoned, but often normal zoning occurs, the Na-content increasing a few percent approaching the contact with the more Na-rich rim. This fact shows that a process of homogeneization has started by which the compositional difference between core and rim has been decreased by a diffusion of CaAl into the rim and NaSi into the core. As a result of this diffusion, a secondary zoning has been produced. As an example, let us consider again the plagioclase sample 282: the composition of the core varies from a value of 17.3% An to about 15.0% near the contact with the rim. The core is large, and was probably formed by a prograde reaction consuming epidote. The rim, of irregular thickness, varies in composition from a minimum of 3% An to a maximum of 7.5% near the contact with the core, proving that diffusion tends to eliminate the compositional gap. If normal zoning were the product of a prograde reaction (as reverse zoning is), the change in composition would probably be more gradual.

Conclusion

As previously observed, K-feldspar as microcline is always present in samples containing normally zoned plagioclase. * Plagioclase is often altered to sericite in the core while the rim is free from alterations. The albitic rims have various thicknesses but generally are more developed at the contact with microcline. In some cases, the rims are found, in the same grain, only in those parts which are close to microcline and not along the boundary with other minerals. Frequently, microcline is more or less perthitic.

These observations support the hypothesis that exsolution of albite from microcline is mostly responsible for the occurrence of normal zoning and sodic rims in the plagioclases of the Oak Lake-Whetstone Lake area.

Oscillatory Zoning

In some epidote-bearing assemblages, the plagioclase shows an oscillatory zoning of the following kind: moving from the center of the grains toward the borders, the An content of plagioclase of sample 123 varies as follows:

1		2		3
An_{15}	→	An_{22}	→	An_{13}
center		intermediate		rim

This oscillatory zoning is the result of the combination of a reverse zoning (1 and 2) and a normal zoning (2 and 3). The reverse zoning is most likely the result of the prograde reaction:

3) epidote + hornblende + quartz $\rightleftarrows$ anorthite + diopside + H_2O

as suggested by Kretz (1963); a later introduction of Na as albite being responsible for the composition of the external rim. Many examples of oscillatory zoning can be explained in this way.

More irregular cases of oscillatory zoning have been found, as, for instance, in sample 167: going from one side to the other of a large plagioclase grain, the following An values have been obtained:

20.5 - 30.8 - 28.0 - 23.9 - 27.5 - 28.5 - 23.4 - 29.8 - 30.0 - 30.7 - 40.7 - 40.2 - 38.7.

The patchy extinction of some of these grains might suggest that they are partly of relic origin (igneous), that homogenization has not been accomplished by recrystallization and that zoning has been further complicated by prograde reactions and retrograde and exsolution phenomena.

Cannon (1966) tries to explain the oscillatory zoning in some plagioclases of the Bartica region as a result of progressive and waning metamorphism and following metasomatism (and possibly varying Na and Ca content of the pore fluids).

Some porphyroblastic plagioclases have grown including part of the matrix and are irregularly zoned, suggesting that replacement of the matrix might have locally influenced the composition of the plagioclase.

V DISTRIBUTION OF SODIUM BETWEEN PLAGIOCLASE AND K-FELDSPAR

Previous Work

The principle on which Barth's geothermometer is based is a direct application of the distribution law which states that for any component present in two phases 1 and 2 at equilibrium, a relationship of the following type exists: $\phi\ (x_1, x_2, P, T) = 0$, where P is the pressure and T the temperature, and any variable can be expressed as a function of the other three.

Applying this principle to the distribution of albite between coexisting feldspars, Barth (1956, 1961, 1962) has demonstrated that for the composition range An_5-An_{35}, the following relationship is true: $\phi\ (x_1/x_2, P, T) = 0$, where $x_1 = Ab/Ab + Or$ in K-feldspar and $x_2 = Ab/Ab + An$ in plagioclase. Neglecting the pressure P which seems to have little effect with respect to the temperature, the following equation is obtained: $x_1/x_2 = K_T$.

The theoretical variation of the distribution ratio with absolute temperature is $K_T = K_1 \dfrac{-(\Delta G)^P_T}{R\ T}$ or $\ln K_T = -\dfrac{1}{T}\ \dfrac{(\Delta G)^P_T}{R} + \ln K_1$, where $(\Delta G)^P_T$ is the free energy change accompanying the passage of one mole of albite from the plagioclase phase to the alkali feldspar phase, K_1 is the coefficient in a standard state and R is the gas constant.

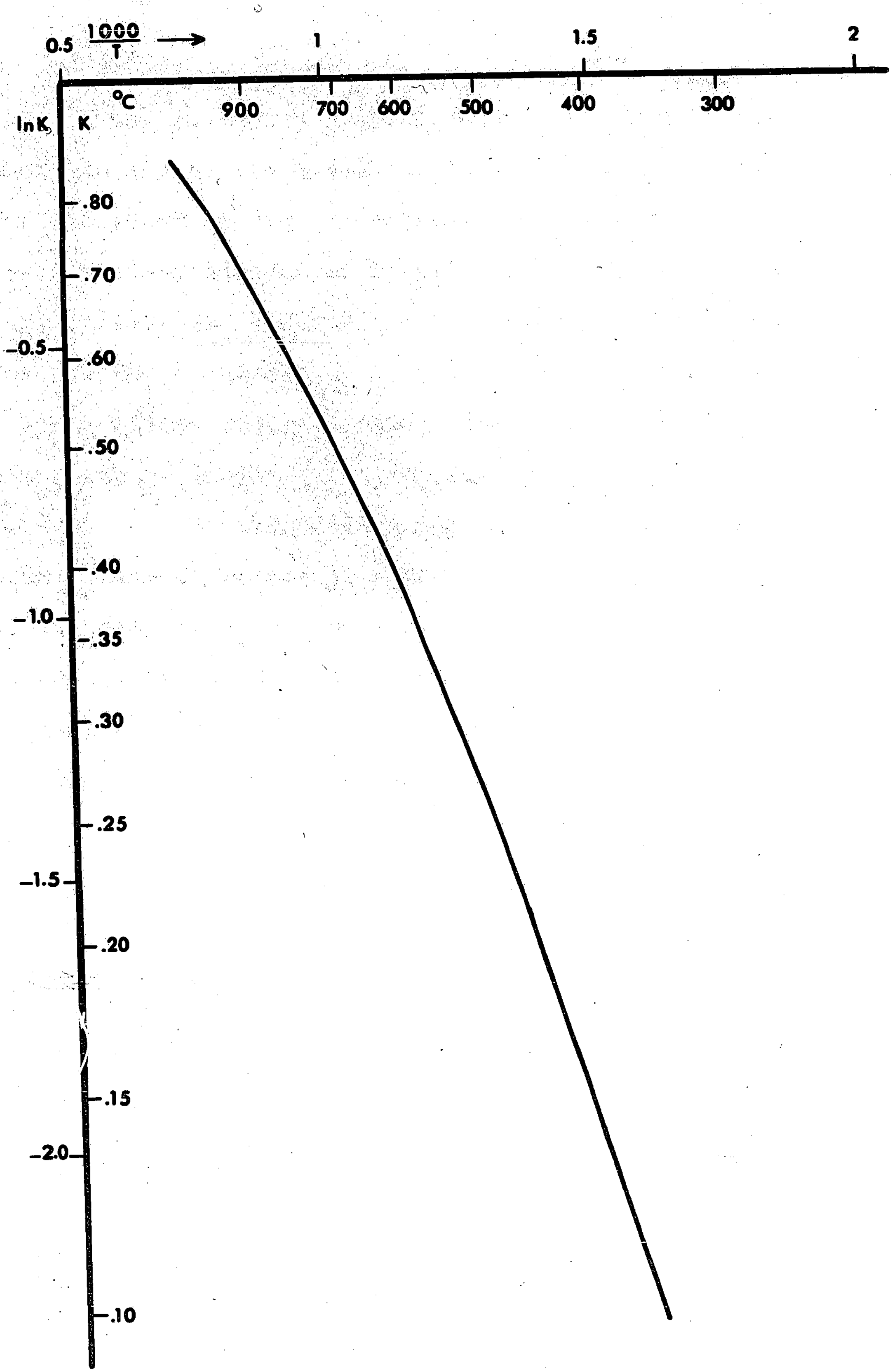
If we neglect the effect of the pressure and if $(\Delta G)_T^P$ is taken as constant over the temperature range of interest to the petrologist, the variation of $1/T$ against $\ln K_T$ gives an almost straight line. In this way, it is possible, knowing x_1 and x_2, to determine K_T and obtain the temperature of crystallization of a rock containing the two feldspars.

Barth constructed this curve (fig. 10) using as a starting point the temperature of formation of trachytes which he estimated at approximately 800° C (the distribution coefficient for the feldspars of these trachytes is 0.6) and arranging the data obtained by other kinds of rocks according to their assumed temperature of formation. The many simplifications and assumptions on which Barth's geothermometer is based made it susceptible to criticism by many authors (Winkler, 1961; Dietrich, 1961 and Orville, 1962). The following points have been particularly stressed by the above-mentioned authors:

1) the temperature values have been fixed by Barth on the basis of unproved empirical data;
2) at best, only the most recent, lowest temperature at which equilibrium existed between feldspar phases can be recorded;
3) the bulk chemical composition influences greatly the K-ratios.

Smith (1965) has determined the distribution of albite among coexisting feldspars of the Clare River and Westport

Fig. 10 - Relation between temperature and the ratio of distribution of albite between feldspar and plagioclase (after Barth, 1956). Abscissa: the inverse of the absolute temperature. Ordinate: natural logarithms to the ratio of distribution.



0.5
1000/T →
1
1.5
2
°C
900
700
600
500
400
300
ln K
K
.80
.70
-0.5
.60
.50
.40
-1.0
.35
.30
.25
-1.5
.20
.15
-2.0
.10

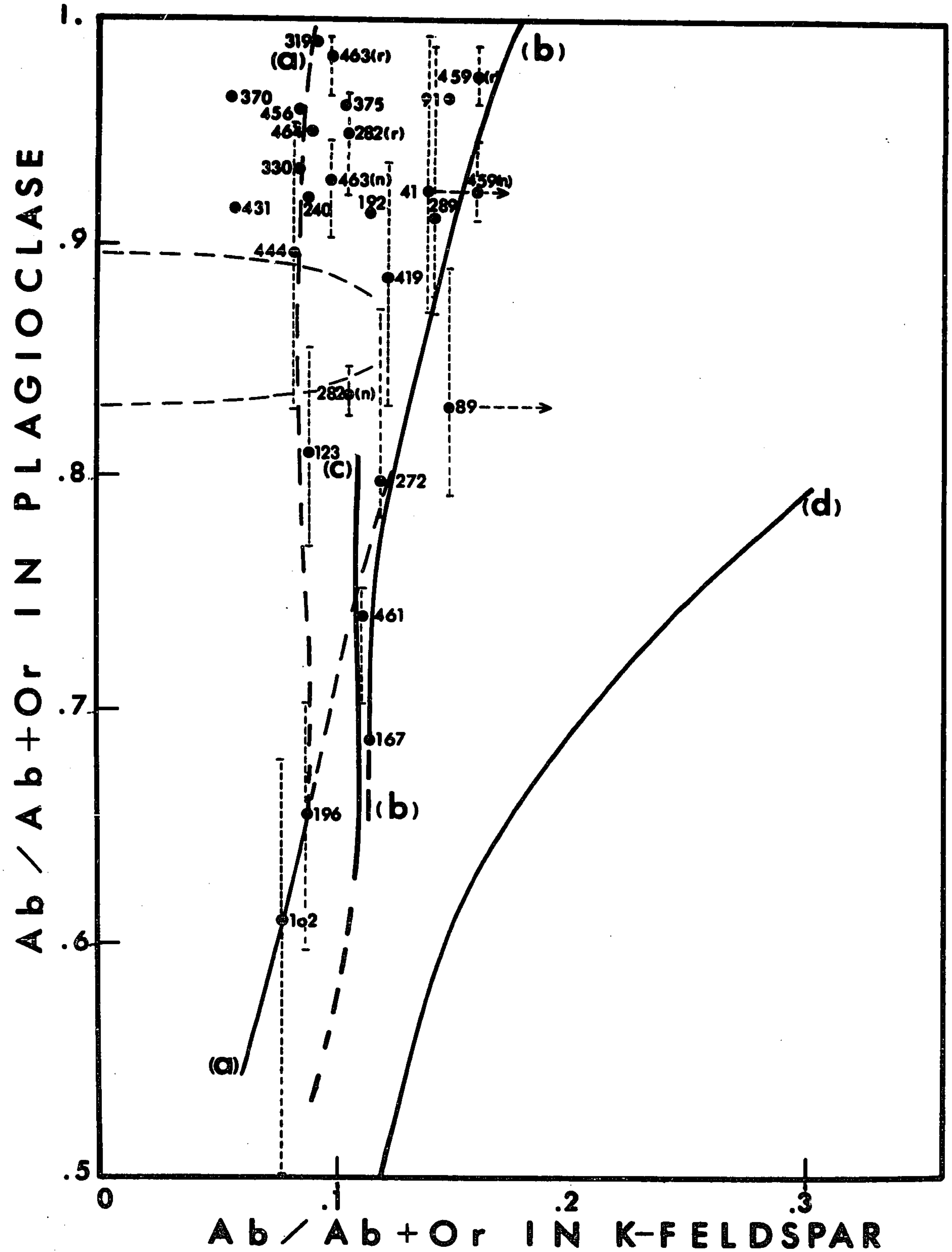
area (Ontario) belonging respectively to the middle almandine amphibolite and to the granulite facies. The distribution curves are shown in fig. 11 together with the curves obtained by the experimental data of Orville (1962) as given by Virgo, of Barth (1962) and Perchuk and Ryabchikov (1968) as given by Fox and Moore (1969).

Virgo (1969) applied Barth's two feldspar geothermometers to the study of rocks from different metamorphic grades in the granulite and almandine facies and on the basis of the results obtained, mainly 1) discrepancies between the temperature inferred by the geological setting and the value obtained by the use of the geothermometer, and 2) wide scattering of values for a single facies and overlap of data from different metamorphic facies within a single area, concluded that, "the major element compositions of coexisting feldspars do not give any indication of their temperatures of crystallization". Virgo (1968) found for the same rocks a regular partition of Sr between feldspars.

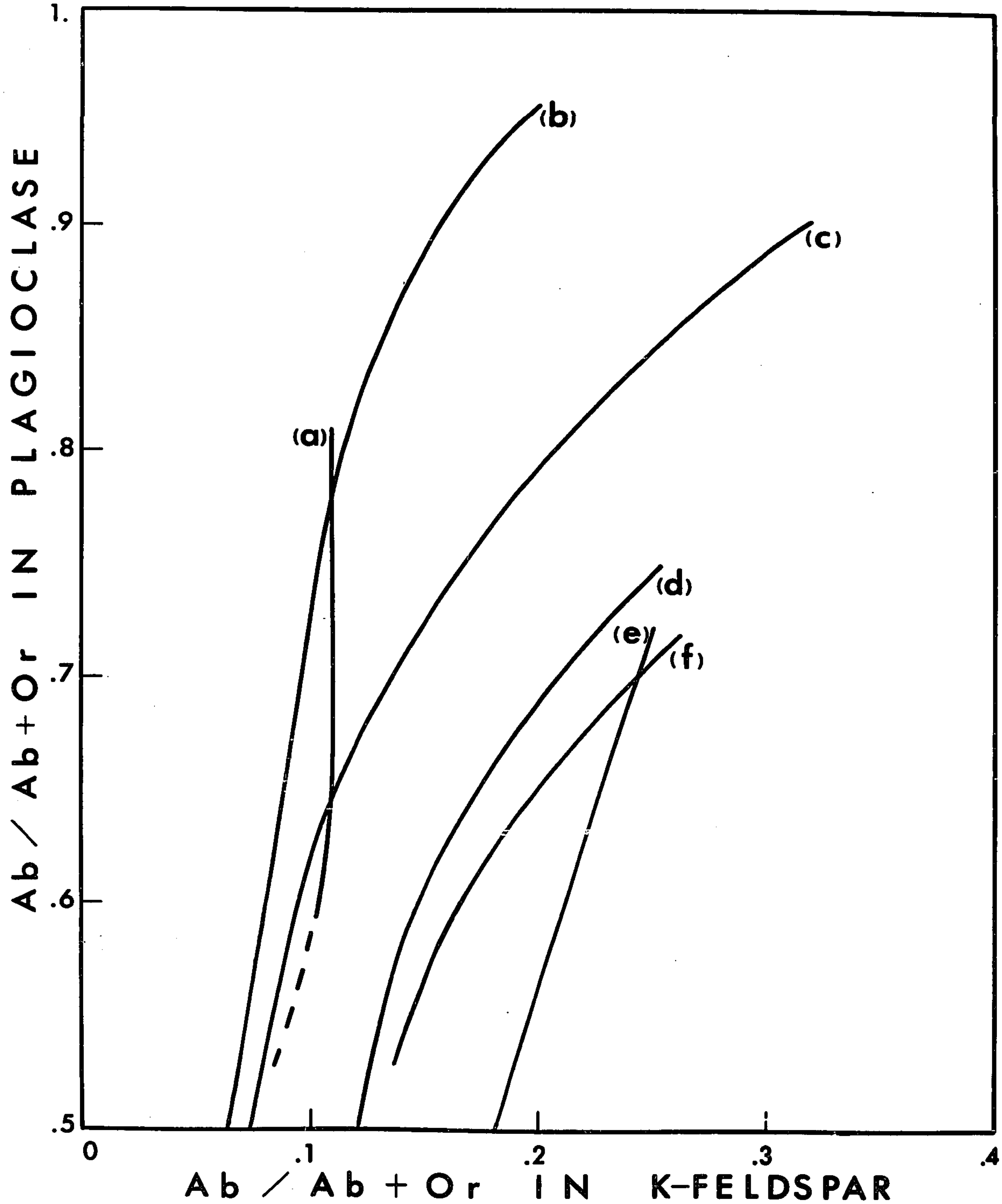
Results of Chemical Analysis

Tables n°5 a and b, pages 53 and 54 and n°6, 7, and 8 pages 89, 90 and 91 give the compositions of the plagioclases and K-feldspars analyzed in the present research. The compositions are expressed in terms of the major feldspar components, Ab, An and Or recalculated to 100%. While the

Fig.11- Distribution of albite between plagioclase and K-feldspar. 11a- Previous results: curves a and d refer respectively to middle almandine amphibolite and granulite facies from Clare River and Westport areas, Ontario (Smith, 1966); curves b and c refer to the 500° and 600°C isotherms of Orville (1962) (after Virgo, 1969), and curves f and e refer to Perchuk and Ryabchikov (1968) and Barth (1962) 600°C isotherms. 11b- Present results for the almandine amphibolite rocks of the Oak Lake-Whetstone Lake area (Ontario). The middle amphibolite and granulite distribution curves of Smith (1966) are also shown (curves c and d). The peristerite solvus has been tentatively drawn. The lower part of curve a and the higher part of curve b have been joined by a dashed line (from sample 196 to 272) to define an isotherm which closely parallels the 500°C isotherm of Orville (1962). Dashed vertical lines: range of An in plagioclases; n: nucleus, and r: rim of zoned plagioclases; the horizontal arrows represent the direction of shifting of the points if the albite exsolved from K-feldspar could be taken into account.



Ab / Ab+Or IN PLAGIOCLASE
Ab / Ab+Or IN K-FELDSPAR
1.
.9
.8
.7
.6
.5
0
.1
.2
.3
(a)
(b)
(c)
(d)
319
463(r)
370
375
456
282(r)
330
463(n)
431
240
41
289
459(n)
459(r)
444
419
282(n)
89
123
272
461
167
196
1o2



1.
.9
.8
.7
.6
.5
0
.1
.2
.3
.4
(a)
(b)
(c)
(d)
(e)
(f)
Ab / Ab+Or IN PLAGIOCLASE
Ab / Ab + Or IN K-FELDSPAR

TABLE 6

Plagioclase Analyses by Atomic Absorption

sample number	Ab	An	Or	SrF
9	73.6	22.9	3.5	.011
28	82.0	16.0	2.0	.023
91	90.5	6.2	3.3	.011
102	69.7	28.0	2.3	.015
240	88.5	7.3	4.2	.018
277	67.2	29.2	3.5	.018
369	81.6	17.3	1.1	.014
370	93.8	3.2	3.0	.009
375	93.0	3.4	3.5	.013
400	70.0	25.4	4.6	.034
407	75.4	21.4	3.1	.032
411	84.0	14.6	1.2	.010
425	93.0	5.8	1.1	.013
428	78.8	19.6	1.6	.038
456	93.7	3.8	2.4	.009
464	91.0	4.6	4.4	.009

TABLE 7

K-Feldspar Analyses by Atomic Absorption

sample number	Ab	Or	An	SrF
91	11.9	86.8	1.1	.009
162	7.4	92.0	.5	.011
172	7.3	91.5	1.12	.012
193	6.8	92.2	.88	.012
196	8.6	90.0	1.4	.008
240	8.6	88.8	2.4	.010
270	4.8	94.8	.36	.005
282	10.4	87.0	2.6	.014
330	6.0	92.5	1.4	.006
370	5.5	93.9	.56	.012
375	10.2	87.2	2.5	.014
414	11.9	85.8	2.3	.015
431	5.6	92.7	1.6	.008
456	8.4	90.6	.94	.008
464	8.8	90.0	1.1	.007

TABLE 8

K-Feldspar Analyses by Microprobe

sample number	Ab	Or	An
41	14.0	85.9	.00
89	16.4	83.5	.00
123	8.8	91.0	.06
167	11.4	88.5	.25
192	11.5	88.5	.00
272	12.14	87.8	.00
289	12.3	87.6	.00
319	9.1	90.8	.03
444	8.3	91.6	.06
447	7.1	92.9	.00
459	16.09	83.9	.00
461	11.0	88.9	.00
463	9.9	90.0	.00

plagioclases of table 5a and 5b have been analyzed by electron microprobe technique and are generally zoned, those of table 6 have been analyzed by atomic absorption and particular care has been taken in selecting unzoned samples. As zoning is a very common characteristic of the plagioclases of the Oak Lake-Whetstone Lake area, most of the samples analyzed are still more or less zoned. The mineral separation technique used which is based on the different specific gravities of minerals gives a final plagioclase concentrate whose composition does not correspond to the average composition of the zoned plagioclase because during the grinding of the sample, grains with different Ab/An ratio are obtained and are separated from each other during the purification by heavy liquids. This procedure necessarily introduces an error in the results.

A major difference results from a comparison of the data of tables 5a and b and 6 with respect to the Or content of the plagioclases analyzed by atomic absorption and electron microprobe techniques. In table 6 the higher orthoclase content is most likely due to the frequent presence of sericite inclusions and K-feldspar impurities.

The higher An content of the K-feldspars analyzed by atomic absorption is also attributed to the presence of impurities such as plagioclase, epidote, apatite, etc. Corrections have not been attempted in both cases.

Discussion and Conclusions

Figure 11b is a plot of Ab/Ab + Or in K-feldspars against Ab/Ab + An in the coexisting plagioclases. The average composition of the plagioclases is represented by a dot and the vertical line shows the range of zoning. As zoning in plagioclases coexisting with K-feldspars is always normal, the lowest part of the vertical lines represents the most calcic composition of the core and the highest part of the lines gives the composition of the rim.

In some cases, zoning is not continuous and the average composition of core and rim is given in figure 11b with their compositional range (samples n° 282, 459,463). In other cases (samples n° 123 and 444), the plagioclases show oscillatory zoning and the extreme compositions have been represented.

As the isotherms, as defined by previous researchers, are very steep in this part of the diagram, zoning of plagioclases (if not very intense) does not greatly affect their position.

The granulite and middle almandine amphibolite isotherms ofSmith (1965) are also shown in the diagram of 11b. The samples lie on the left side of the granulite isotherm of Smith in the areadelimited by the two lines a and b.

Not many data are available for the lower part of the diagram but the trend observed by Smith for the middle amphibolite facies is parallelled by lines a and b as drawn in figure 11b. The lack of points in the interval of X_{Ab} values .84 - .9 for plagioclases is related to the existence of the peristerite solvus which has been tentatively drawn. More data close to this compositional range are required to define more precisely its exact position. In the higher part of the diagram, the two lines diverge and a great scattering of points can be observed.

Scattering is expected to occur as a result of variation in metamorphic grade from lower to upper amphibolite facies, but no relationship exists in the present case between the position of the points and their metamorphic grade. The samples which lie close to line b all belong to higher metamorphic zones: 41 and 89, for instance, are in the K-feldspar-sillimanite zone while 289 and 459 are in the upper sillimanite zone.

The K-feldspars of samples 41 and 89 are highly perthitic and intense exsolution of albite must have sensibly decreased the Ab/Ab + Or ratio. The real position of these samples on the diagram, if the Na lost by exsolution could be taken into account, would shift to the right toward the granulite facies isotherm of Smith.

The scattering of points can be related to the Na content of the K-feldspars. Samples which have been collected at a short distance from each other and do not differ in their plagioclase composition, are widely dissimilar in the Na-content of their K-feldspars (see, for instance, the pairs 456-459 and 370-375).

The normal zoning or albitic rims of plagioclases have been interpreted as a product of exsolution of Ab from K-feldspar which in some cases is obviously perthitic. Often the exsolutions are preferentially located along the border of the grains showing a tendency of the two feldspar phases to segregate, the albite migrating outside the grain. This is also confirmed by the fact that generally the sodic rims are found in plagioclases at the contact with K-feldspar and not with other minerals.

If exsolution of Ab from K-feldspar is responsible for the normal zoning of plagioclase, the composition of both feldspars must have changed, the average Ab content of plagioclase having increased and that of K-feldspar having decreased as a result of unmixing. The points representing the composition of the coexisting feldspars before exsolution must then lie below and to the right of the points in the diagram of figure 11b and the shifting depends on the extent of exsolution.

Notwithstanding the occurrence of unmixing in K-feldspars and zoning in plagioclases, which account for most of the scattering, agreement exists between the trend found by Smith for the middle amphibolite facies and the results of the present research.

VI DISTRIBUTION OF SODIUM AND POTASSIUM AMONG FELDSPAR PHASES AND MICA

Previous Work

Eugster and Yoder (1954-55) studied the feldspar-mica equilibria in the system K-feldspar - albite - corundum - water and presented their results in the isothermal sections of figure 12 which are based on experimental data at 30,000 psi water pressure. The subsolidus relations on the muscovite-paragonite join (fig. 13) have been determined experimentally by Eugster and Yoder (1954-55), who used the feldspar solvus of Bowen and Tuttle to express the composition of feldspars in equilibrium with muscovite at 500° and 600° C.

Some important conclusions can be drawn by considering the data of figures 12 and 13.

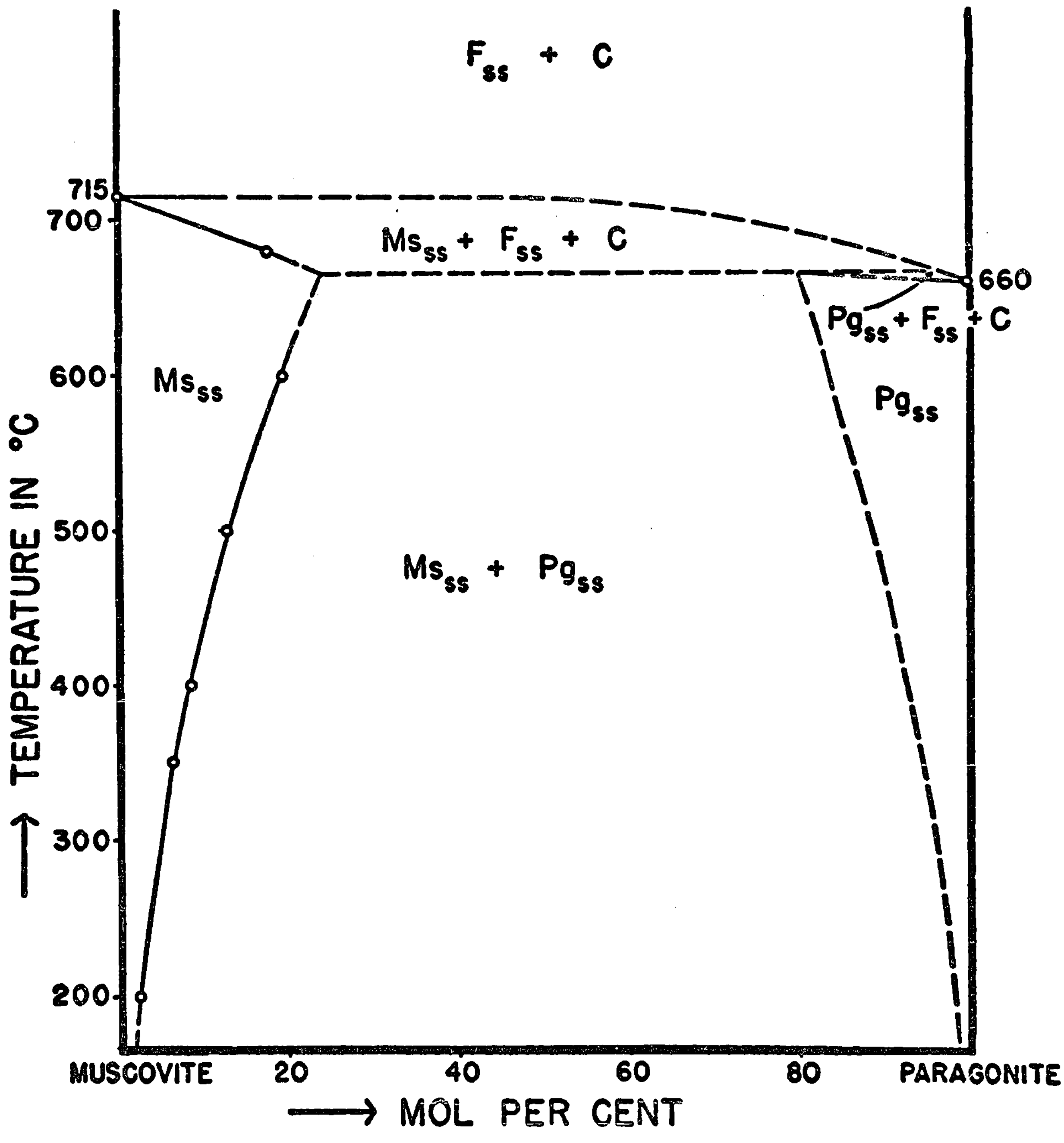
1) the extent of solid solutions increases in both micas and feldspars with increasing temperature until below 650° C the feldspar solvus closes and only one felspar occurs.

2) the Na content of muscovite increases with temperature only as long as paragonite is present. Paragonite becomes unstable before muscovite and breaks down according to the reaction:

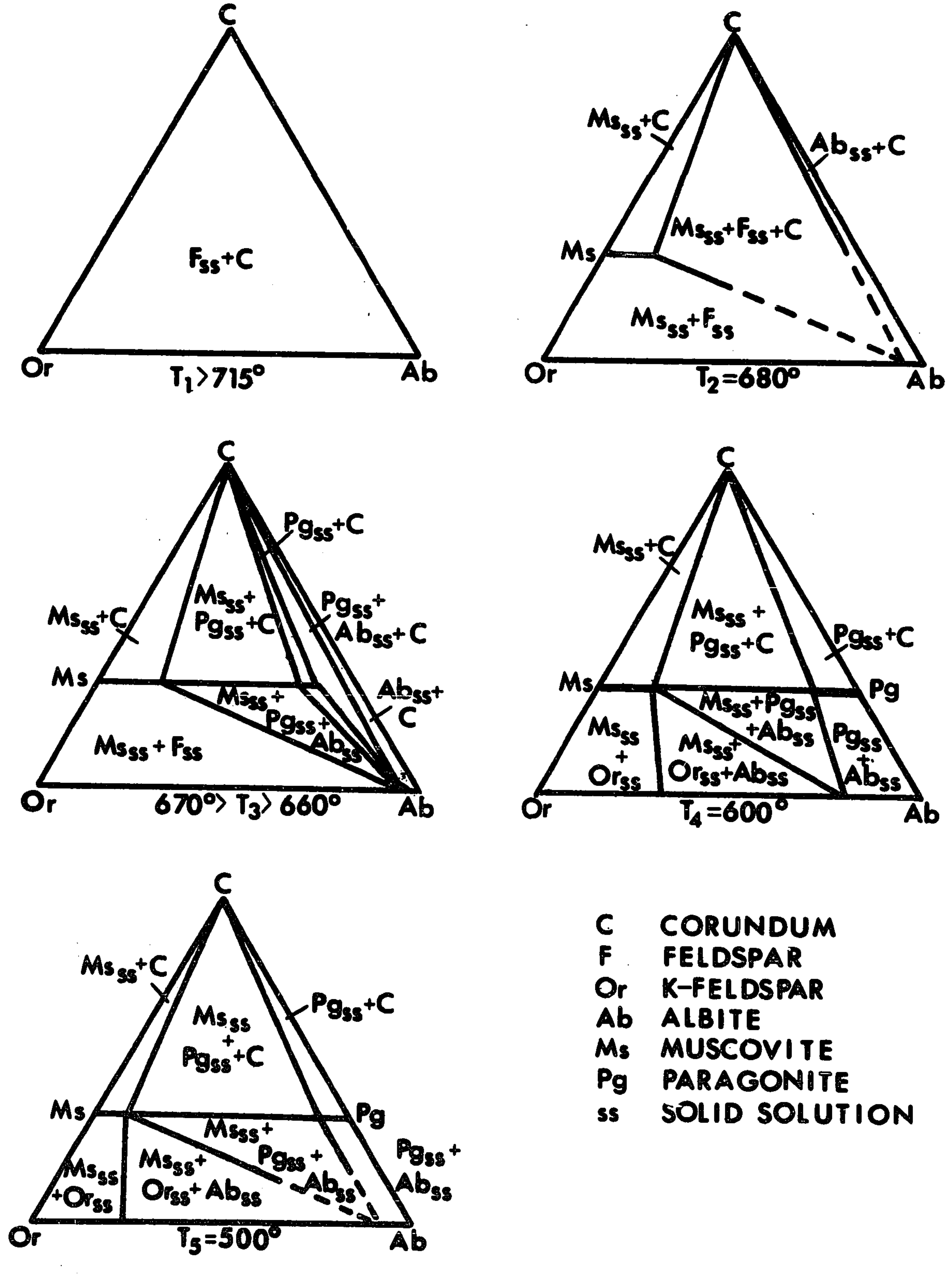
$$1)\ \underset{\text{paragonite}}{NaAl_2(OH)_2Si_3AlO_{10}} \rightleftarrows \underset{\text{albite}}{NaAlSi_3O_8} + \underset{\text{corundum}}{Al_2O_3} + \underset{\text{water}}{H_2O}$$

Fig. 12 - Mineral assemblages in the system albite-potassium feldspar-corundum-water at selected temperatures and 30,000 psi water pressure (after Eugster and Yoder, 1954-55). The hydrous phases are projected onto the albite-potassium feldspar-corundum plane.

Fig. 13 - Preliminary phase diagram for the subsolidus region of the muscovite-paragonite join (after Eugster and Yoder, 1954-55).



F_{ss} + C
715
700
Ms_{ss} + F_{ss} + C
660
Pg_{ss} + F_{ss} + C
600
Ms_{ss}
Pg_{ss}
500
Ms_{ss} + Pg_{ss}
400
300
200
→ TEMPERATURE IN °C
MUSCOVITE
20
40
60
80
PARAGONITE
→ MOL PER CENT


C
$F_{ss}+C$
Or
$T_1 > 715°$
Ab
C
$Ms_{ss}+C$
$Ab_{ss}+C$
$Ms_{ss}+F_{ss}+C$
Ms
$Ms_{ss}+F_{ss}$
Or
$T_2 = 680°$
Ab
C
$Pg_{ss}+C$
$Ms_{ss}+$
$Pg_{ss}+C$
$Pg_{ss}+$
$Ab_{ss}+C$
$Ms_{ss}+C$
Ms
$Ms_{ss}+$
$Pg_{ss}+$
Ab_{ss}
$Ab_{ss}+$
C
$Ms_{ss}+F_{ss}$
Or
$670° > T_3 > 660°$
Ab
C
$Ms_{ss}+C$
$Ms_{ss}+$
$Pg_{ss}+C$
$Pg_{ss}+C$
Ms
Pg
$Ms_{ss}+Pg_{ss}$
$+Ab_{ss}$
Ms_{ss}
$+$
Or_{ss}
$Ms_{ss}+$
$Or_{ss}+Ab_{ss}$
Pg_{ss}
$+$
Ab_{ss}
Or
$T_4 = 600°$
Ab
C
$Ms_{ss}+C$
$Pg_{ss}+C$
Ms_{ss}
$+$
$Pg_{ss}+C$
Ms
Pg
$Ms_{ss}+$
$Pg_{ss}+$
Ab_{ss}
$Ms_{ss}+$
$Or_{ss}+Ab_{ss}$
Ms_{ss}
$+Or_{ss}$
$Pg_{ss}+$
Ab_{ss}
Or
$T_5 = 500°$
Ab
C CORUNDUM
F FELDSPAR
Or K-FELDSPAR
Ab ALBITE
Ms MUSCOVITE
Pg PARAGONITE
ss SOLID SOLUTION

at a temperature of 660° C and a water pressure of 30,000 psi. After the disappearance of paragonite, the extent of Na solid solution in muscovite progressively decreases with increasing temperature, Na-rich muscovite becoming unstable before K-rich muscovite. Evans and Guidotti (1966) suggest that the reaction taking place at this point in quartz-bearing assemblages is:

2) $NaAl_2(OH)_2Si_3AlO_{10} + SiO_2 \rightleftarrows NaAlSi_3O_8 + Al_2SiO_5 + H_2O$

paragonite component of muscovite	quartz	albite component of plagioclase	sillimanite	water

by which muscovite becomes progressively enriched in K and albitic rims are produced in plagioclase.

Guidotti (1963) and Evans and Guidotti (1966) discuss the feldspars-micas equilibria in the system Na_2O - K_2O - CaO - Al_2O_3 - SiO_2 - H_2O. Following Thompson (1957), they disregard SiO_2 as a compositional variable on the grounds that it is generally present in excess as quartz and H_2O which is considered as a completely mobile, externally controlled component. The equilibria can then be represented in a tetrahedron with K-feldspar, albite, anorthite and sillimanite at the corners. Evans and Guidotti discuss particularly the reactions taking place at the K-feldspar-sillimanite isograd but give an exhaustive account of the changes occurring during progressive metamorphism above the paragonite-quartz stability field (fig. 14). Diagrams a, b and c give the phase relations within the tetrahedron: sillimanite - orthoclase - albite - anorthite a) well below the K-feldspar-sillimanite isograd, b) just below the isograd, and c) above the isograd.

The following observations are of particular interest:

1. Presence of a two phase field muscovite-albite (or muscovite-plagioclase) which separates the three phase fields muscovite-sillimanite-albite (or plagioclase) and muscovite-orthoclase-albite (or plagioclase).

2. Muscovite in equilibrium with sillimanite and albite (or plagioclase) is more Na-rich than muscovite in equilibrium with orthoclase and albite (or plagioclase).

3. With increasing temperature, the K-feldspar-sillimanite tie line appears as a result of the reaction:

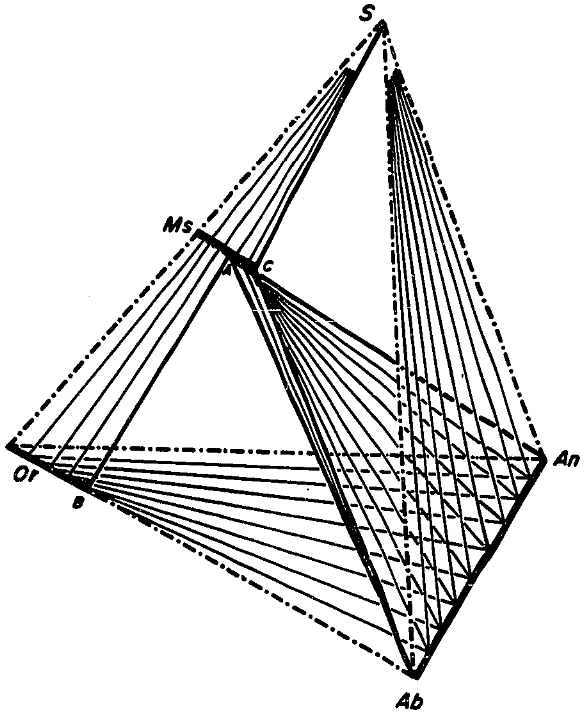
3) quartz + muscovite + sodic plagioclase $\rightleftarrows$ sillimanite + Na-rich microcline + more calcic plagioclase + H_2O.

by which the most sodic muscovite cannot any longer coexist in equilibrium with pure albite but with a plagioclase containing some anorthite and a four-phase field muscovite - plagioclase - orthoclase - sillimanite appears.

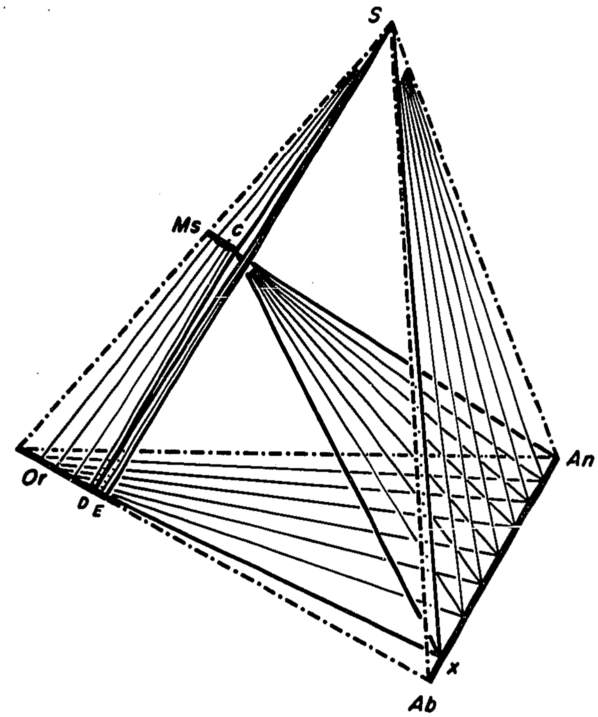
Mineral Assemblages

In the present research, all the assemblages but two

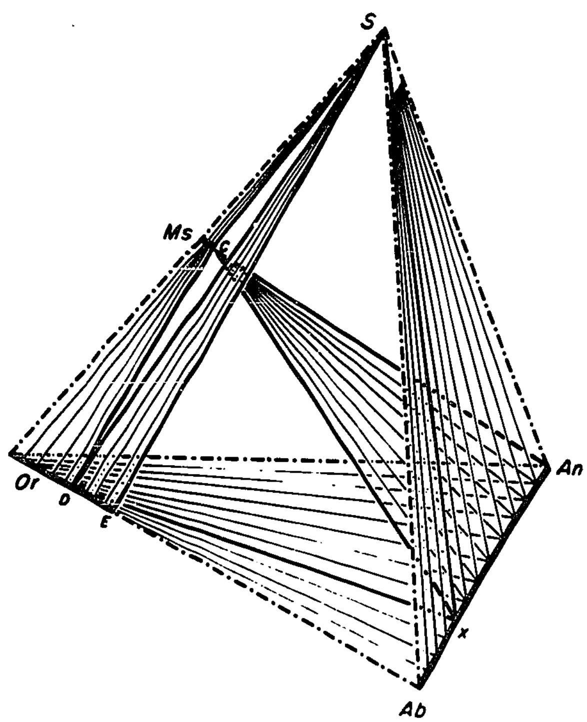
Fig. 14 - Phase relations within the tetrahedron: sillimanite-orthoclase-albite-anorthite (after Evans and Guidotti, 1966).



a



b



c

lie in the field: 1) muscovite - quartz - plagioclase; 2) muscovite - quartz - plagioclase - microcline; 3) quartz - plagioclase - microcline. Only two samples which were collected outside the Oak Lake-Whetstone Lake area, 41 (at Blue Mountain) and 89 (at Coe Hill) have the assemblage: muscovite - quartz - plagioclase - microcline - sillimanite and belong to the K-feldspar-sillimanite zone.

According to the results of Evans and Guidotti (1966), it is expected that:

1) at the same metamorphic grade, muscovites of assemblage 1 are more Na-rich than muscovites of assemblage 2, and

2) the Na content of muscovites and microclines of assemblage 2 increases with the metamorphic grade.

The Sodium Content of Mica and Feldspars

A plot of Na/Na + K ratios in coexisting muscovite and feldspars in a K_2O-Na_2O-Al_2O_3 diagram does not show the expected relationships and the Na-content of muscovite and K-feldspar cannot be correlated with the kind of assemblage and the degree of metamorphism The occurrence of perthite and the presence of normal zoning in plagioclase (which has been interpreted as a product of exsolution from K-feldspar) are most likely responsible for the lack of correlation between K-feldspar composition and metamorphic grade.

The muscovites coexisting with plagioclase have, on the average, a higher amount of Na with respect to muscovites coexisting with two feldspars. This relationship becomes more evident if the assemblages are divided into two groups:

1) muscovite - quartz - albite ± microcline, and
2) muscovite - quartz - plagioclase (An > 10%) ± microcline.

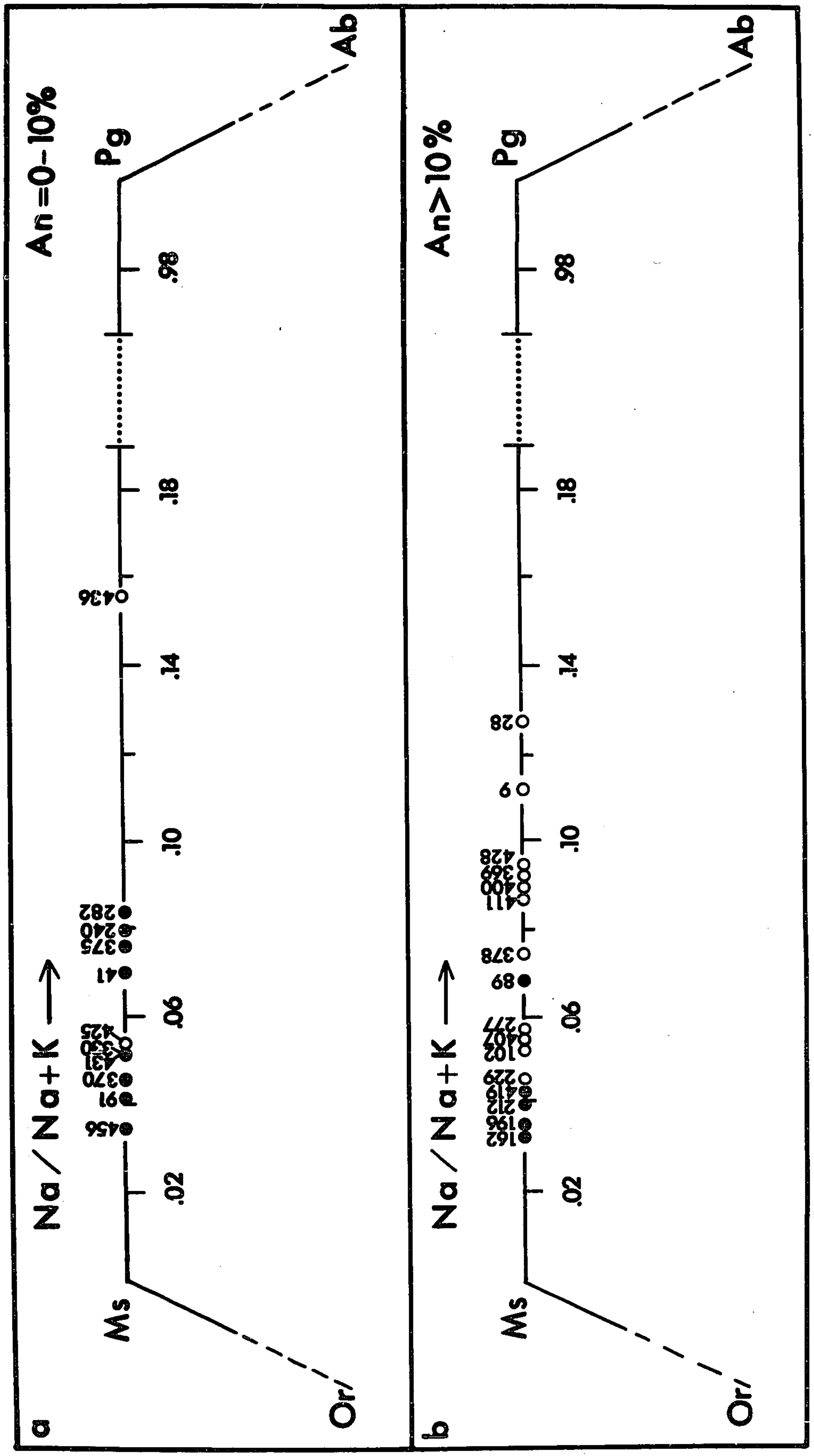
Figure 15 shows the composition of muscovites on the join muscovite - paragonite in the assemblages 1 (fig. 15a) and 2 (fig. 15b). The full dots represent the muscovites coexisting with two feldspars, and the open ones, the muscovites coexisting only with albite or plagioclase.

While in figure 15a only two samples (425 and 436) do not contain microcline and one (425) is anomalously low in Na-content, figure 15b shows a better relationship, the extent of paragonite solid solution being higher when microcline is not present. Ms 229 is probably retrograde and Ms 89, which belongs to the K-feldspar-sillimanite zone, displays, as expected, a lower Na-content than the lower grade assemblages muscovite-plagioclase.

The Effect of Compositional Variables

The presence of various amounts of anorthite in plagioclase and of Fe and Mg in muscovite (which is generally phengitic) could be partly responsible for the observed

Fig. 15 - Composition of muscovites on the join muscovite-paragonite. The full dots represent the muscovites coexisting with two feldspars and the open ones, the muscovites coexisting with plagioclase. The plagioclases of figure 15a are albites and those of figure 15b contain more than 10% anorthite.


a
An=0-10%
Na / Na+K ⟶
Ms
Pg
Or
Ab
.02
.06
.10
.14
.18
.98
456
91
370
431
320
425
41
375
240
282
436
b
An>10%
Na / Na+K ⟶
Ms
Pg
Or
Ab
.02
.06
.10
.14
.18
.98
162
196
212
419
229
102
404
277
89
378
411
400
369
428
9
28

scattering of data.

The anorthite content of plagioclase

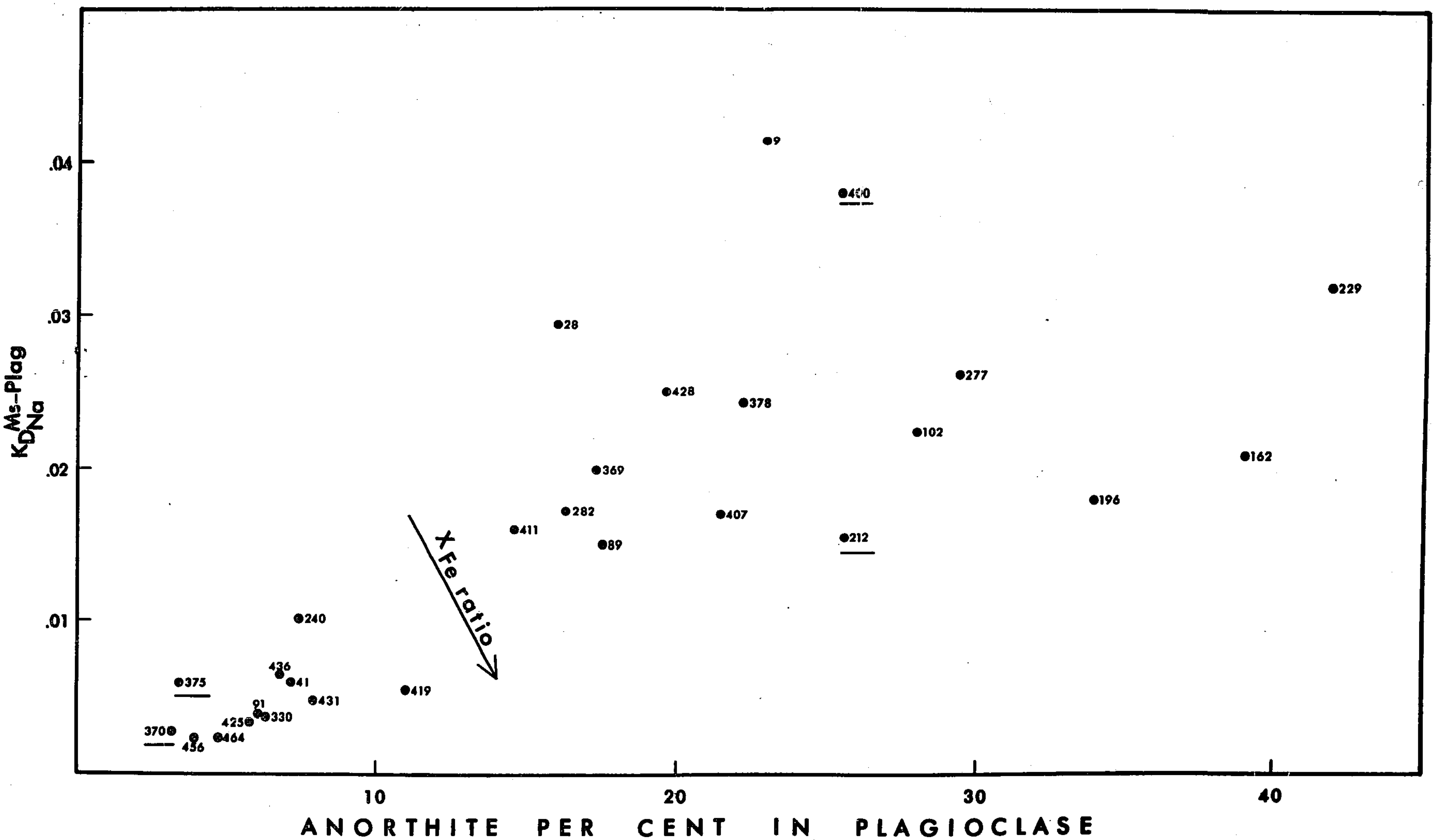
Figure 16 shows a plot of $K_{D_{Na}}^{Ms-plag}$ as a function of the An content of plagioclase with $K_{D_{Na}}^{Ms-plag} = \dfrac{X_{Na}^{Ms}(1 - X_{Na}^{plag})}{X_{Na}^{plag}(1 - X_{Na}^{Ms})}$, with X_{Na} = Na/Na + K + Ca.

Although a great scattering of points exists, a general increase of K_D with the An content of plagioclase can be observed, the lowest K_D values belonging to the muscovite - albite pairs. The peristerite gap separates muscovite-albite from muscovite-plagioclase (An > 10%) assemblages.

The X_{Fe} Ratio of mica

The way in which the presence of Fe and Mg in muscovite affects its Na-content and the K_D values can be determined by comparing the composition of pairs of micas which, coming from samples collected at a short distance from each other, can be assumed to have recrystallized at approximately the same temperature and pressure. Two of such pairs will be considered which are of particular interest because in each pair, the An-content of the coexisting plagioclase is the same and only the effect of the phengitic component on the K_D values can then be evaluated.

Fig. 16 - Plot of $K_{D_{Na}}^{Ms\text{-}plag}$ as a function of the anorthite content of plagioclase. The direction of increasing X_{Fe} values in the muscovites is also shown.



.04
.03
.02
.01
$K_{D_{Na}}^{Ms-Plag}$
10
20
30
40
ANORTHITE PER CENT IN PLAGIOCLASE
X_{Fe} ratio
9
490
229
28
277
428
378
102
369
162
282
407
196
411
89
212
240
436
375
41
419
431
91
330
425
370
464
456

Table 9 gives the composition of the pairs of muscovites 370-375 and 212-400, in terms of Na_2O, total iron (as Fe_2O_3) and MgO. The X_{Fe} = Fe/Fe + Mg ratios and the $K_{D_{Na}}^{Ms-plag}$ values are also given.

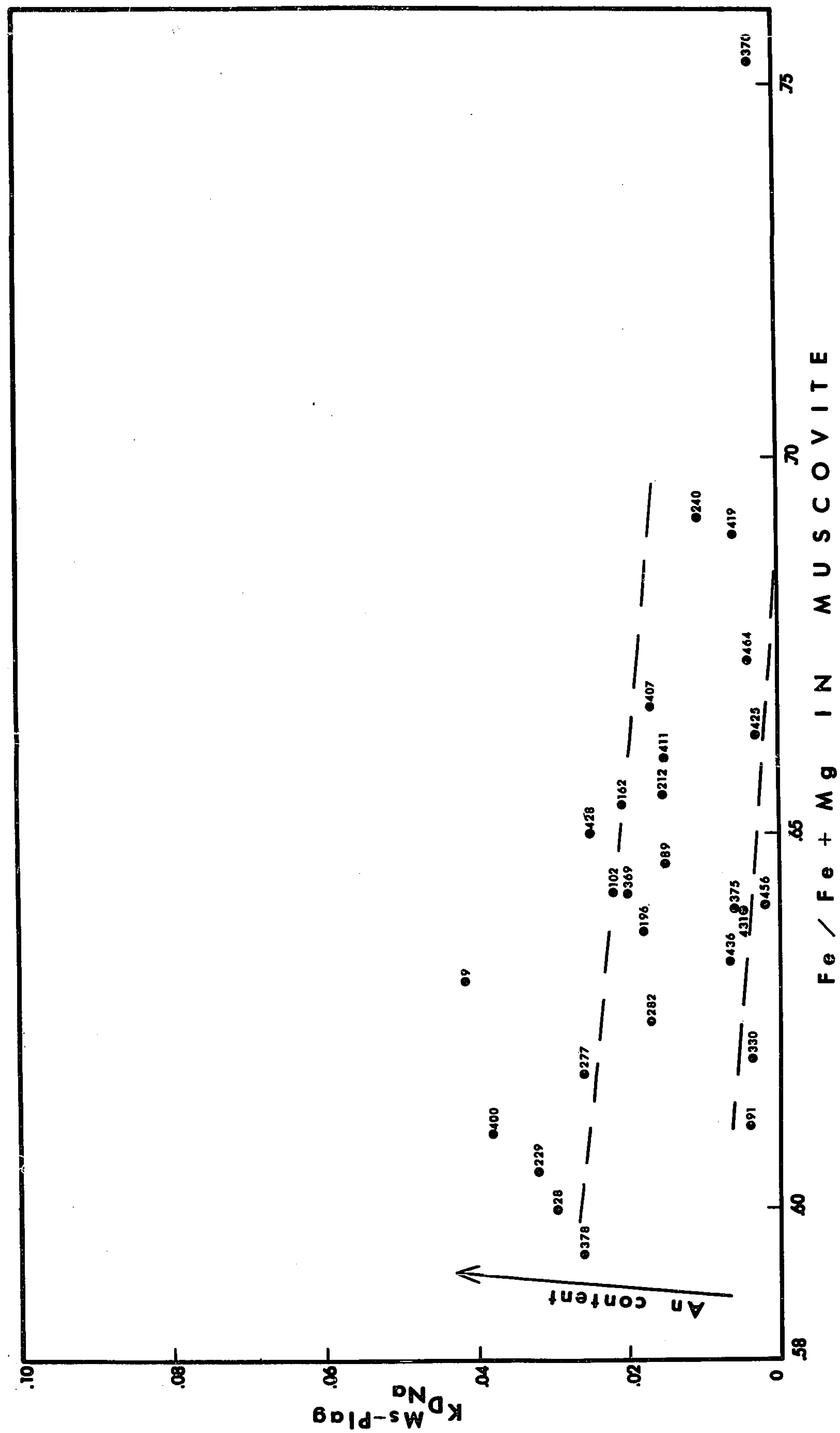
Table 9.

	Na_2O	Fe_2O_3	MgO	X_{Fe}	K_D
370	.34	5.11	.84	.75	.003
375	.61	2.67	.76	.64	.006
212	.29	5.24	1.39	.65	.015
400	.62	3.30	1.07	.61	.038

Inside each pair, the micas with the highest Fe_2O_3 + MgO and X_{Fe} values have the lowest Na_2O content and the corresponding K_D values are also lower. If this relationship is true, the affinity of Na for muscovite is highly affected by the amount of elements such as Fe and Mg and by their atomic ratios. The four samples considered in table 9 have been underlined in figure 16 and the arrow shows the direction of change of K_D with increasing (Fe + Mg) and X_{Fe} in muscovite.

Figure 17 is a plot of $K_{D_{Na}}^{Ms-plag}$ against the X_{Fe} ratio of muscovite. Two trends approximately parallel each other and show a decrease of K_D values with increasing X_{Fe}. The lower trend corresponds to the pair muscovite-albite and the second, lying above it, corresponds to the pair muscovite-plagioclase (An > 10%). The peristerite gap separates

Fig. 17 - Plot of $K_{D_{Na}}^{Ms-plag}$ as a function of the X_{Fe} ratio in muscovite. The direction of increasing anorthite content in plagioclase is also shown.



Fe / Fe + Mg IN MUSCOVITE
$KD^{Ms-Plag}_{Na}$
An content
.58
.60
.65
.70
.75
0
.02
.04
.06
.08
.10
370
240
419
464
407
425
411
212
162
428
89
102
369
375
456
431
196
436
9
282
277
330
400
91
229
28
378

the two groups of points. The scattering inside each group depends on, 1) different An content and presence of zoning in plagioclase, 2) different T and P conditions, and 3) other compositional variables such as $Fe^{2+}/(Fe^{2+} + Fe^{3+})$, TiO_2, Mg/Fe^{2+}, etc. which might presumably affect K_D.

Summary and Discussion

In the previous pages, both the An content of plagioclase and the X_{Fe} ratio of muscovite have been found to affect K_D: at constant T and P, an increase of K_D being equally obtained by increasing An or decreasing X_{Fe}; and the effect of such compositional variables obscures the effect of the metamorphic grade.

Some cases of interest will now be discussed and a few examples will be given to show the effect of the interaction of An and X_{Fe} on K_D. Temperature will be considered constant in each case. Given two samples (1 and 2) which belong to the same metamorphic grade and contain muscovite and plagioclase, the following possibilities may occur:

1) T = constant

   An = constant

   $X_{Fe_1} \neq X_{Fe_2}$

In this case, X_{Fe} is the only variable and K_D changes accordingly. If $X_{Fe_1} > X_{Fe_2}$, $K_{D_1} > K_{D_2}$. See samples 370-375, 400-212, 102-212.

2) T = constant

X_{Fe} = constant

$An_1 \neq An_2$

Here, if $An_1 > An_2$, $K_{D_1} > K_{D_2}$.

3) T = constant

$An_1 \neq An_2$

$X_{F_e} \neq X_{F_e}$

Two possibilities must be considered:

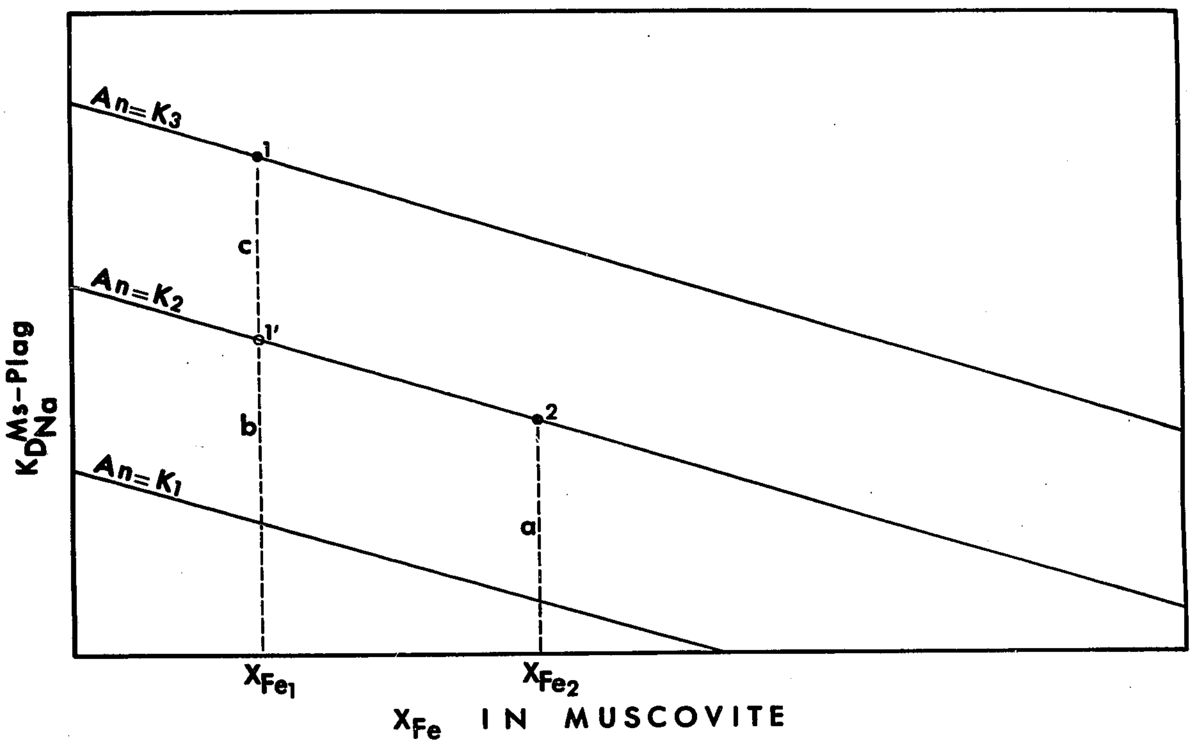
3a) If $An_1 > An_2$ and $X_{Fe_1} < X_{Fe_2}$, then $K_{D_1} > K_{D_2}$.

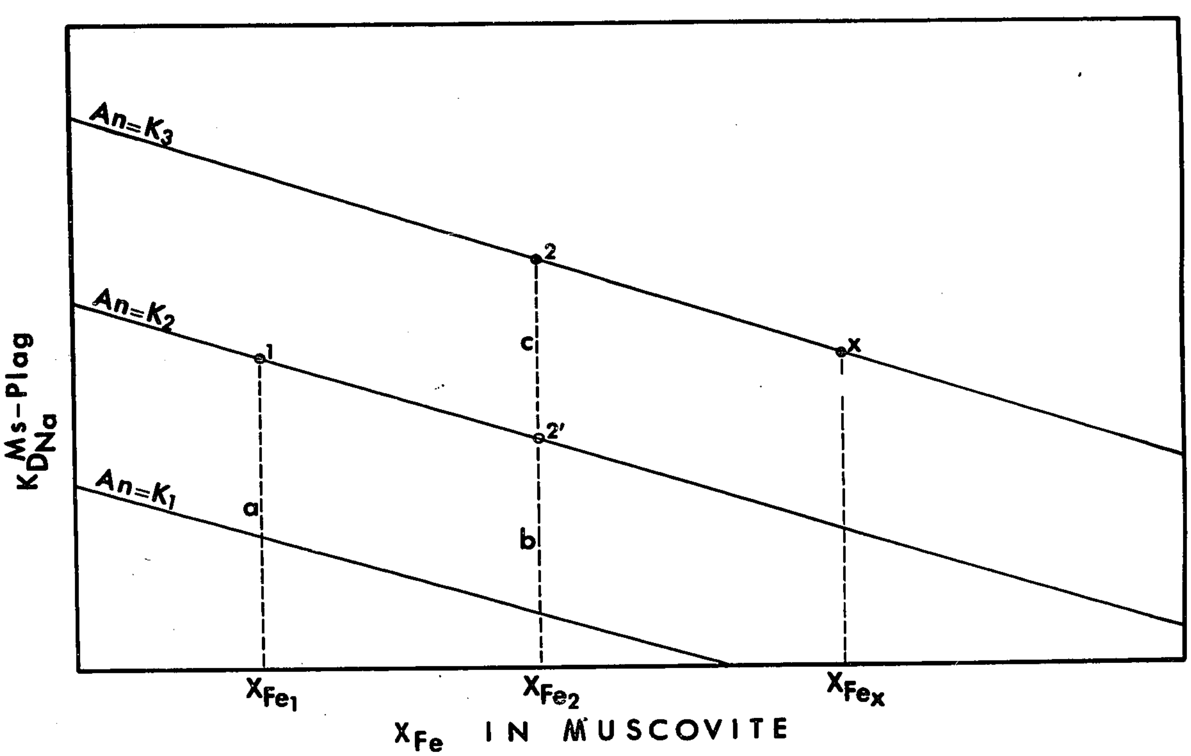
In fact, both variables have the effect of increasing the value of the distribution coefficient $K_{D_{Na}}$ of sample 1 with respect to sample 2. This is shown in figure 18a where 1 and 2 which have different X_{Fe} values have been represented as lying on two lines of anorthitic composition K_2 and K_3 (with $K_3 > K_2$). If 1 and 2 had the same An value, for instance K_2, then the difference in their K_D's would be $K_{D_1} - K_{D_2} = b - a$. An increase of An from K_2 to K_3 further increases this difference to the final value $(b + c - a)$. See, for instance, the pairs 282-277 and 229-196.

3b) If $An_1 < An_2$ and $X_{Fe_1} < X_{Fe_2}$, K_D can be >, =, or < K_{D_2}.

In this case, K_{D_2} tends to be increased by the higher An

Fig. 18 - Relationship between $K_{D_{Na}}^{Ms\text{-}plag}$ and X_{Fe} in muscovite when: a) $An_1 > An_2$, and $X_{Fe_1} < X_{Fe_2}$; and b) $An_1 < An_2$ and $X_{Fe_1} < X_{Fe_2}$.


An=K3
An=K2
An=K1
1
1'
2
c
b
a
$K_{D_{Na}}^{Ms-Plag}$
X_{Fe_1}
X_{Fe_2}
X_{Fe} IN MUSCOVITE


An=K3
An=K2
An=K1
1
2
2'
x
c
b
a
$K_{D_{Na}}^{Ms-Plag}$
X_{Fe_1}
X_{Fe_2}
X_{Fe_x}
X_{Fe} IN MUSCOVITE

value, and decreased by the higher X_{Fe_2}. In figure 18b the decrease of K_{D_2} induced by X_{Fe_2} is eliminated by the high difference in An content and $K_{D_2} - K_{D_1} = c + b - a$ becomes > 0, therefore, $K_{D_2} > K_{D_1}$.

Only for values of $X_{Fe_2} > X_{Fe_x}$, $(K_{D_2} - K_{D_1})$ becomes < 0 and $K_{D_2} < K_{D_1}$.

The pairs of samples 102-378, 91-89, 419-425, 431-428 and 378-400 show the relationship discussed in this last case.

VIII CONCLUSIONS

The present research has been concerned with the study of the effects of changes of metamorphic grade and bulk composition on the minerals in some metamorphic rocks of the Grenville province. The mineral equilibria considered are, 1) muscovite + biotite, 2) plagioclase + epidote, 3) K-feldspar + plagioclase and 4) two feldspars + muscovite. The results may be synthesized and summarized as follows:

1) The partitioning of Na, total Fe, Mg, Mn, Li and Ti among coexisting muscovite and biotite shows that equilibrium has been approached in the distribution of these elements. Two different trends have been identified, corresponding to the assemblages phengite-biotite and muscovite-biotite. Both assemblages are present over the whole range of metamorphic grades considered and their occurrence is related to the bulk composition of the host rock. In the case of the distribution of Mn, the total amount of Mn in micas has been proved to be affected by the presence or absence of other Mn bearing minerals, such as epidote or garnet. The amounts of Fe^{2+}, Fe^{3+} and of Al present in tetrahedral and octahedral coordination have not been determined. These data would give a more complete knowledge of the equilibrium among micas and, by allowing the use of atomic ratios such as $Fe^{2+}/(Fe^{2+} + Mg)$, $Fe^{2+}/(Fe^{2+} + Mg + Fe^{3+} + Al_{VI} + Ti)$ etc.

could reduce the scattering of some distribution diagrams.

The present study confirms that the effect of the metamorphic grade is subordinate to that of bulk composition and thus only by considering an isochemical series of rocks affected by prograde metamorphism will it be possible to study the influence on the equilibria of the metamorphic grade alone.

2) The plagioclase-epidote equilibrium necessarily involves the participation of other phases as the reaction: anorthite + $H_2O \rightleftarrows$ clinozoisite is not balanced. In this research, an attempt has been made to integrate textural with chemical data; components such as Fe^{3+} in epidote, phengite in muscovite, almandine in garnet, etc. have also been considered. In general, the Al-component of the epidote molecule reacts according to different reactions (depending on the paragenesis), producing anorthite molecules, and the epidote becomes enriched in the Fe^{3+} component. This has been suggested by 1) the high anorthite content of the plagioclases coexisting with epidote relative to those not coexisting with epidotes, and 2) the reverse zoning of plagioclases, and the zoning of epidotes which show a decrease of Al-content toward the border of the grains. Sphene, magnetite and ilmenite have been shown to participate in most equilibria and the Fe^{2+}/Fe^{3+} ratio in the host rock seems to be particularly important. In some reactions (see, for instance,

reaction 12 (p.60), a change of this ratio and an increase of p_{O_2} in the vapor phase has been suggested. A knowledge of the value of the Fe^{2+}/Fe^{3+} ratio in the minerals participating in the various reactions as well as a study of zoning in minerals such as garnet, hornblende, biotite, muscovite, etc. would be very important in achieving a more complete knowledge of the reactions occurring in rocks containing the mineral pair plagioclase-epidote.

The composition of the volatiles must play an important role in the breakdown reactions of epidote as H_2O and CO_2 are involved in most reactions, suggesting the dependence of the equilibrium temperature on the particular value of the CO_2/H_2O ratio.

The plagioclase and epidote composition at a certain temperature is a function of the mineral paragenesis: in fact, each reaction of breakdown of epidote takes place at different P and T conditions according to the particular assemblage present.

Some assemblages which have not been studied because of lack of analytical data suggest that other reactions must occur in quartz-free plagioclase and epidote-bearing rocks which have been found in some parts of the area.

3) The distribution of albite between two feldspars is in agreement with the results obtained by Smith (1967) for the middle almandine amphibolite facies. The presence of normal

zoning in the plagioclases coexisting with microcline has suggested that exsolution of albite from K-feldspar has occurred. This fact has been considered responsible for the scattering observed in figure 11b, p. 88.

4) The distribution of Na and K between muscovite and plagioclase has been shown to be highly dependent on compositional variables such as Fe/Fe + Mg in muscovite and An in plagioclase. Other variables which have not been considered such as Fe^{2+}/Mg, Fe^{2+}/Fe^{3+}, TiO_2, etc. could also affect the distribution of Na and K.

Due to the presence of exsolution in K-feldspar, the equilibrium muscovite-microcline has not been studied. Work on this equilibrium would show if the partition of Na and K is affected by the variables considered above.

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APPENDIX 1

Methods of Analysis

Mineral Separation

The samples analyzed for the present research have been crushed to the size at which the amount of composite grains was reduced to a very small proportion: in the case of feldspars, in many instances, it was necessary to use a grain size between 325 and 400 mesh.

The preliminary separation of mica from mica-rich rocks was made by passing the powder over sheets of cardboard to which the mica adhered more readily than quartz and feldspar. The separation of muscovite from biotite was then accomplished by means of a Frantz magnetic separator and gravity methods. Heavy liquids of different density were obtained by mixing Bromoform with Dimethyl Sulphoxide or Methylene Iodide. The minerals were finally purified by hand picking.

When the amount of micas was too small, a rough concentration was obtained by passing the powder several times through the magnetic separator; at low field current, the first mineral to separate was biotite (if garnets and epidotes were not present). The current was then increased to extract interleaved muscovite-biotite flakes and composite grains; and finally increased again to separate the remaining muscovite from quartz and feldspar. The final portion was then run at high field current until a pure mixture of quartz and feldspars was obtained. The different fractions were then purified by gravity methods and hand picking.

The separation of the feldspars was accomplished by gravity methods. Microcline was easily separated from quartz + plagioclase + composite grains because of its lower density, but it was not possible to obtain a pure plagioclase separation. The composite grains containing fragments of microcline were eliminated by gradually increasing the density of the liquid. The plagioclase density in the compositional range of the samples studied is very close to that of quartz; for this reason, a weighted mixture of quartz and plagioclase was analyzed and the amount of plagioclase present in the mixture was determined from the Ab, Or and An values obtained from the analysis, the excess weight being considered as quartz.

Atomic absorption technique

The minerals, purified and washed carefully in acetone, were ground in an agate mortar and dried in oven at 110° C for 1-2 hours. After allowing the samples to cool down to room temperature for 10-15 minutes in a dessicator, 100 milligrams of powder were weighted in a platinum crucible or Teflon beaker (previously cleaned and dried). The sample was then humidified with a few drops of distilled water and dissolved into 10 ml of hydrofluoric acid and 1 ml of perchloric acid. The crucible was then placed on a hot plate to allow complete evaporation at the temperature of 70° C; this operation was repeated at least twice until complete disgregation of the sample was obtained. After the final evaporation, the residuum was dissolved in a 1 normal solution of perchloric acid and the final volume was made up to 100 ml. The solutions obtained in this way were analyzed for Na, K, Ca, Fe, Mg, Mn, Li and Sr using a Techtron model AA-4 atomic absorption spectrophotometer. All determinations were made in duplicate; the reference solutions were prepared from Fisher's standard solutions. Two mineral standards (Na- and K-feldspars) and a rock standard (andesite) were also taken into solution and included with the analyses, thus giving an estimate of the accuracy of the analytical method which can be evaluated from table 10. The solutions of the minerals were subdivided in different portions and opportunely diluted and treated to avoid interferences as follows:

TABLE 10

Concentration Values Found and Recommended in Alkali Feldspars and Andesite Standards

	99a* Na Feldspar		70a* K Feldspar		AGV1+ Andesite	
	Given	Found	Given	Found	Given	Found
Fe	.046	.045	.053	.049	4.65	4.61
MgO	.020	.022	-	-	1.50	1.54
CaO	2.14	2.11	.11	.09	-	-
Na_2O	6.2	6.0	2.55	2.52	-	-
K_2O	5.2	5.3	11.80	11.79	-	-

* 70a, 99a, National Bureau of Standards mineral standards

\+ AGV1, United States Geological Survey rock standard

The precision of the method, listed as per cent of the amount present is:

± 2% Na_2O, ± 2% K_2O, ± 5% Cao (if present in high amounts);

± 5% Na_2O, ± 5% K_2O, ±10% CaO (if present in low amounts);

± 2% MgO, ± 3% Fe_2O_3, ± 3% MnO, ± 10% Li_2O.

100 mg in 100 ml →
- Li, Na, K, Fe (if low)
- 10 ml diluted to 100 ml: Na, K, Fe (if high)
  - ↓ 20 ml + 2 ml 7% La solution: Ca, Mg (if high)
- 20 ml + 2 ml 7% La solution: Sr, Ca, Mg (if low)

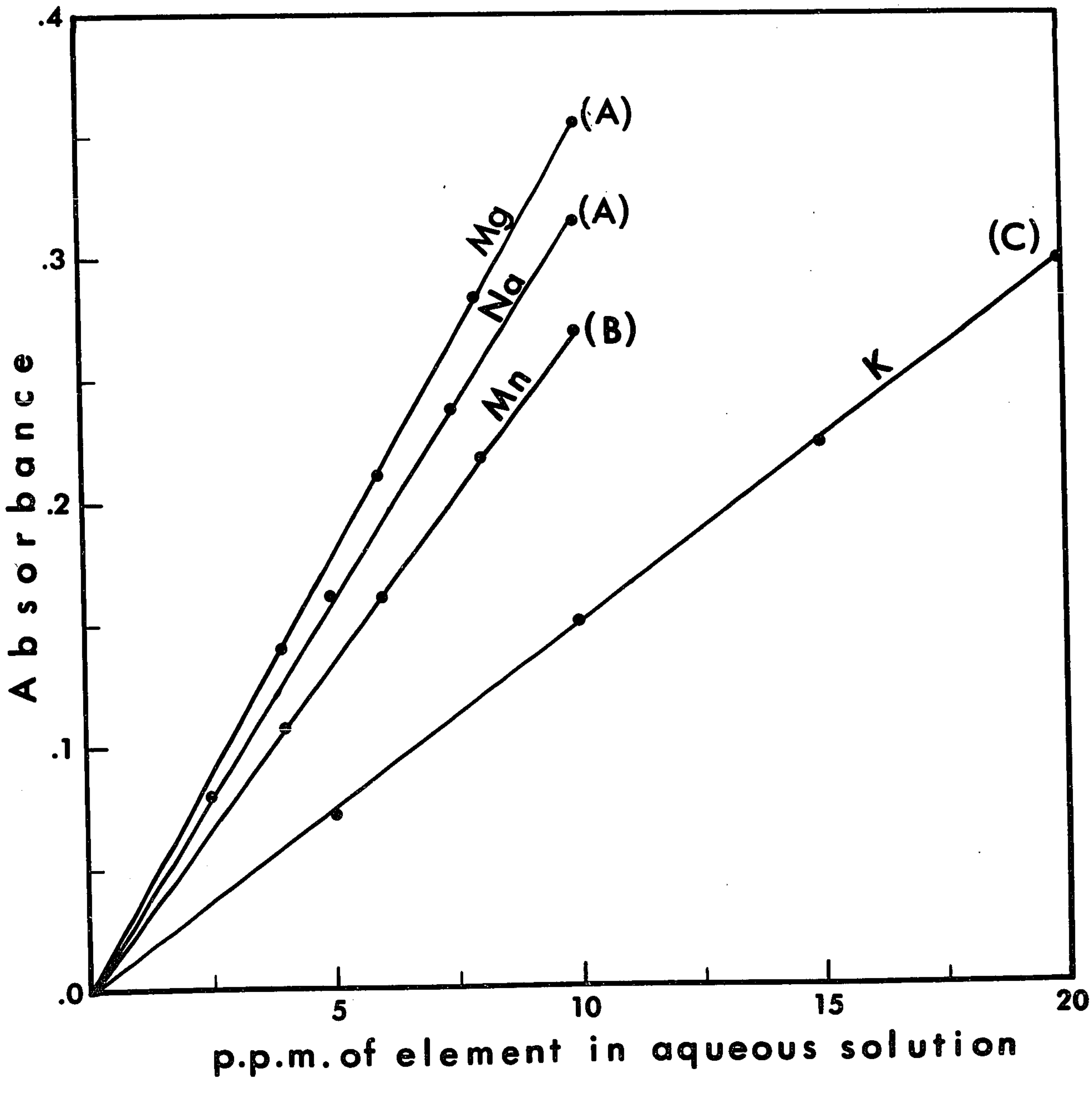
Some calibration curves are given in fig. 19(a, b and c).

Electron microprobe technique

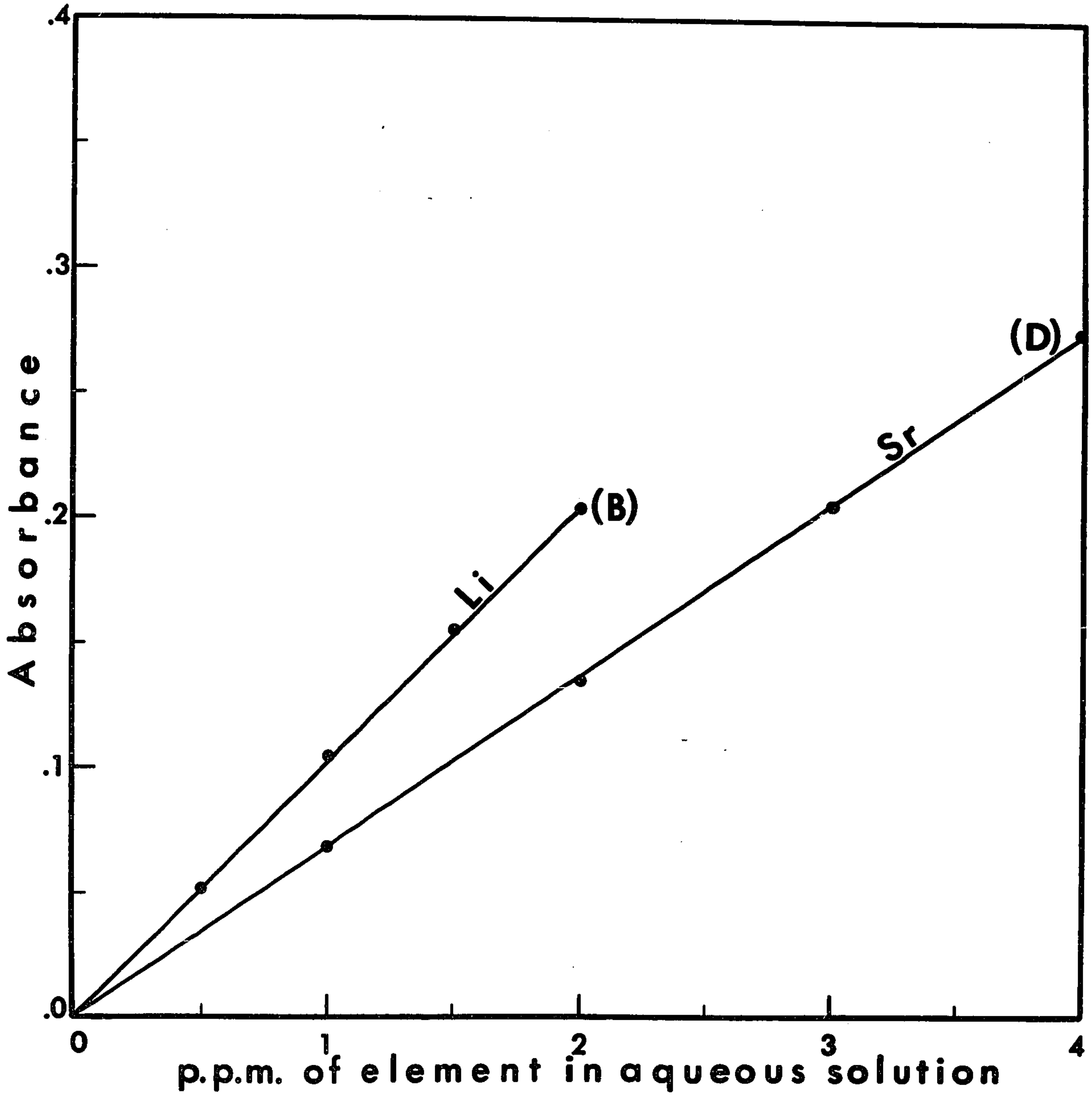
An A.R.L. electron probe microanalyser was used to determine the amounts of Al and Ti in 12 muscovites and 19 biotites, of Ca, Na, K, Fe, Mg, Mn, Al and Ti in 15 epidotes and Na, Ca and K in 31 plagioclases and 13 microclines. The following standards were used: biotite (for Al and Ti), albite (for Na), orthoclase (for K), anorthite (for Ca), spinel $Mg\,Al_2\,O_4$ (for Mg) and metallic Fe and Mn.

The analysis of zoning in plagioclase and epidote was preceded by an attentive study of the polished thin sections. Large grains were selected for analysis among those which displayed a marked pattern of zoning. At least five grains for each mineral were analyzed in each section, scanning across each grain and taking readings at approximately the same intervals.

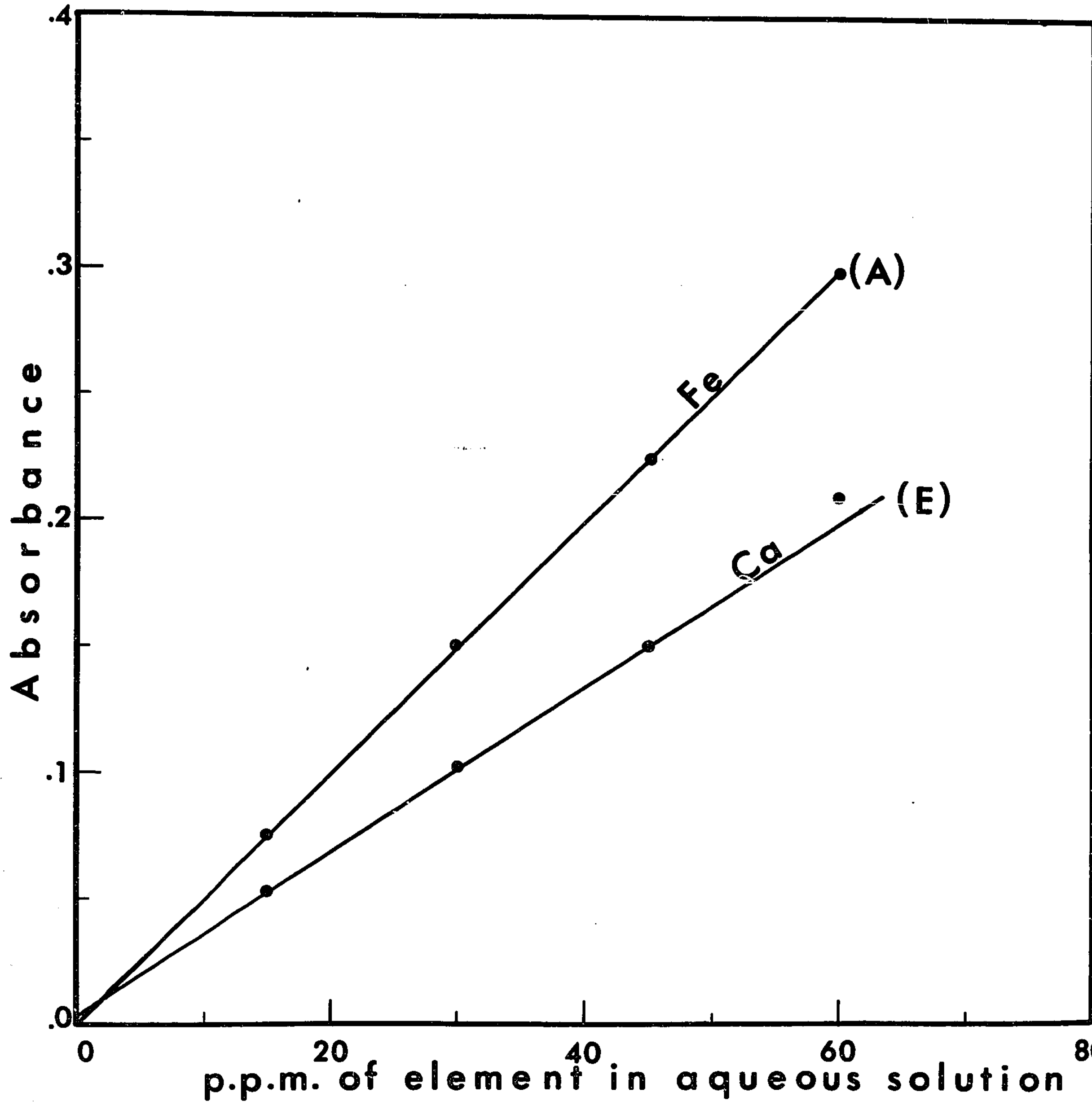
The instrumental conditions were: accelerating potential 15 Kv and integration time 10 seconds; the sample current was varied according to the concentration of the elements



.4
.3
.2
.1
.0
5
10
15
20
Absorbance
p.p.m. of element in aqueous solution
Mg
Na
Mn
K
(A)
(A)
(B)
(C)



.4
.3
.2
.1
.0
Absorbance
0
1
2
3
4
p.p.m. of element in aqueous solution
Li
(B)
Sr
(D)


.4
.3
.2
.1
.0
0
20
40
60
80
Absorbance
p.p.m. of element in aqueous solution
Fe
Ca
(A)
(E)

analyzed. Loss of Na and K from plagioclase and microcline was avoided by using a beam diameter of 15 micron.

The following corrections have been employed:

EMX: correction for dead time of detector system (dead time constant assumed: 2.50 x 10^{-6} sec.); correction for drift from standard to standard; subtraction of background readings from standards and specimens. →

→ half processed data

EMX_2: absorption (Frazer's computer fit for absorption coefficients; Philibert's absorption correction). Heinrich's sigma value.

fluorescence (K-K, K-L, L-K, L-L, $\alpha - \beta$, $\alpha - \alpha$, $\beta - \alpha$, $\beta - \beta$) from Reed.

atomic number effects (from Duncumb and Reed) →

→ final results.

APPENDIX 2

The modal composition of the rock samples selected for the present study is given in table 11. The following abbreviations have been used:

Q	=	quartz
Plag	=	plagioclase
KF	=	K-feldspar (microcline)
Ms	=	muscovite
Bi	=	biotite
Ep	=	epidote
G	=	garnet
Hbl	=	amphibole (mostly hornblende)
Chl	=	chlorite
Cc	=	calcite
Sill	=	sillimanite
St	=	staurolite
Sph	=	sphene
Op	=	opaque minerals (magnetite, ilmenite)

Apatite, tourmaline, zircon, rutile are generally present in small amounts.

TABLE 11

Modal Composition of the Samples

sample number	Q	Plag	KF	Ms	Bi	Ep	G	Hbl	Chl	Cc	Sill	Sph	Op
9	20	30		10	30				5	1			4
15		25				14		55				5	1
25	20	20	10	10	35					1			4
28	20	30		10	20		5		8	5			2
41	25	5	20	20	25						5		
42	20	30			34		15						1
89	20	20	10	5	35		5				5		
91	25	15	28	25	5								2
95		65			35								
102	25	15		25	18			5		10			2
123*		30	3			25		24		3		1	4
167**	20	15	24			10		15				1	3
162	25	5	10	20	14	14				5		2	5
172	15	25	30			5		8		7		5	5
192		40	30		5			20		3			2
193		35	25		10			25		3			2
196	20	10	28	15	20	1				2			4
197***	10	2			30	18	8	4		5		5	8
199****	20	28			10	5	5	20		2		3	5
212	35	14		12	20	10				5		1	3
213	35	25	5	5	15	10				3			2
229	40	5		4	15	25			1	2		3	5
240	30	15	24	15	4	3	3	2		1		1	2
255	35	20			5	20		10		5		2	3
257	20	15				15	8		40			1	1
270	32	24	38	1									5
272	20	30	10		10	5				10		5	10
277	15	35		5	23	1				5		1	15
282	20	30	20	5	15	13						1	6

TABLE 11 (cont.)

sample number	Q	Plag	KF	Ms	Bi	Ep	G	Hbl	Chl	Cc	Sill	Sph	Op
289	25	27	35		3								10
309	24	10			28	15				18		4	1
319	45	30	18	2									5
330	35	10	15	22	15								3
369	30	25		10	20					3		2	10
370	40	30	17	10			1						2
375	25	20	10	30	14						1		
378	25	20		25	15	5				15			5
382	28	20			18	10		3		15		2	4
400	35	20		8	15				10	10			2
407	45	15		15	10					1		1	13
411	35	30		5	15		2			3			10
414	40	20	5		20			10				1	4
419	34	15	10	14	15	1				3		3	5
425	40	25		10	10					9		1	5
428	30	25		15	15				5	5			5
431	30	30	10	7	5				3	2		3	10
436*****	20	25		18	12		4						1
444	35	25	15	5	23								2
447	30	20	40	5	2								3
456	30	25	35	5									5
459	30	30	30	2	5								3
461	15	34	5		35	6		1				1	3
463	35	20	30	2	10		1						2
464	35	20	30	8								1	6

* diopside = 10
** diopside = 12
*** scapolite = 10
**** sulphide = 2
***** staurolite = 20

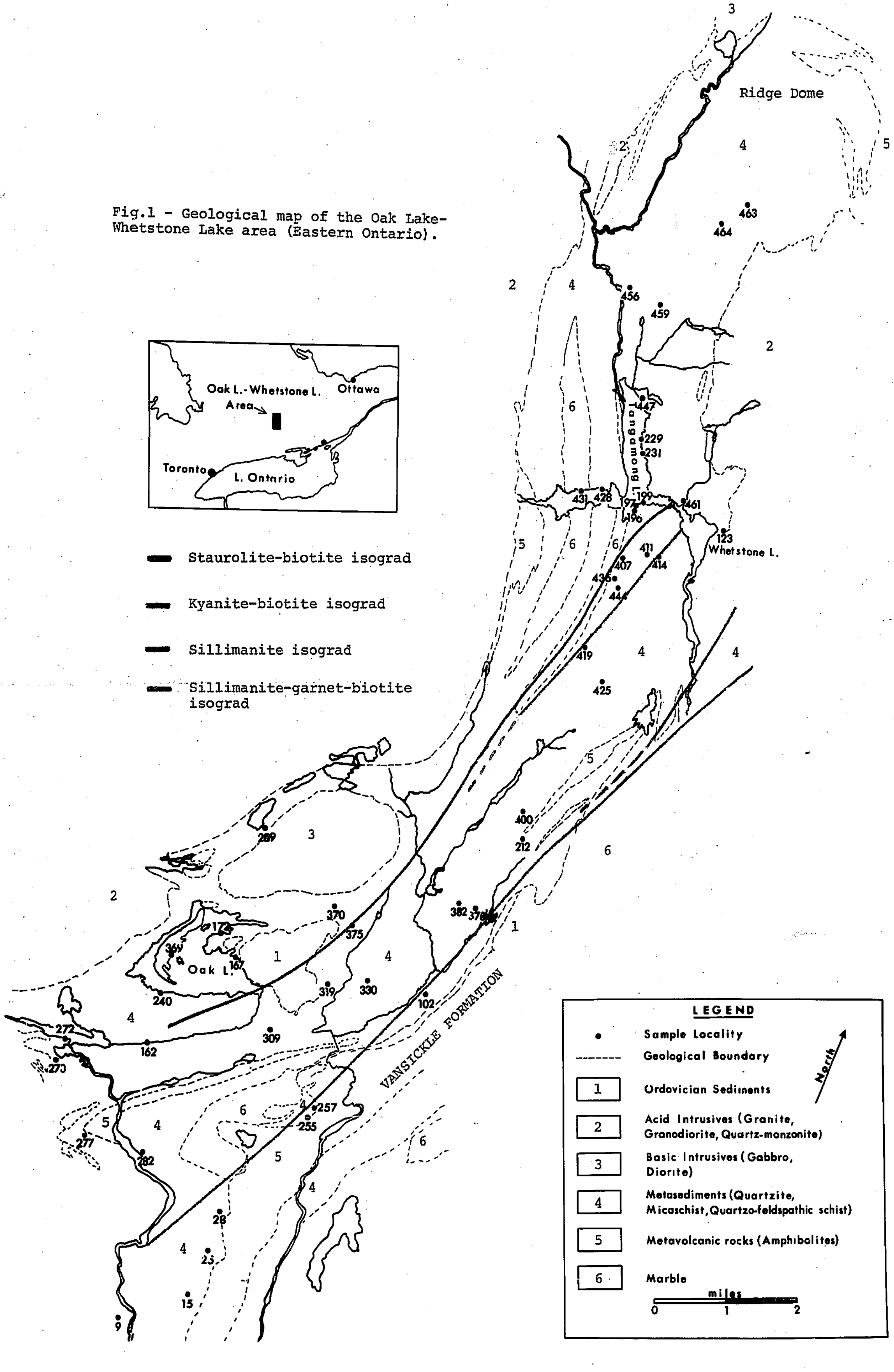


Fig.1 - Geological map of the Oak Lake-Whetstone Lake area (Eastern Ontario).