

# COMPOSITION AND GENESIS OF PYROXENE AND GARNET RELATED TO ADIRONDACK ANORTHOSITE AND ANORTHOSITE-MARBLE CONTACT ZONES\*

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## ABSTRACT

The genesis of some pyroxenes and garnets related to Adirondack anorthosite, anorthosite-marble contact zones and their metamorphic equivalent are discussed on the basis of 10 clinopyroxenes whose chemical analyses as related to optical properties have recently been presented by Hess, and upon one new orthopyroxene analysis and 7 new garnet analyses given here. It is found that the clinopyroxenes of the anorthositic rocks are high in alumina as compared with those of gabbro. In contact zones with marble, ferrosalite and grossularite-andradite skarn is developed on the marble side whereas an almandite-rich mafic gneiss is often found as a border facies on the anorthositic side. One sheet of salite gabbro is interpreted as the product of assimilation of ferrosalite skarn by gabbroic anorthosite magma.

## INTRODUCTION AND ACKNOWLEDGMENTS

The author made a collection of Adirondack minerals for a systematic study of their chemical composition as related to the igneous rocks and their metamorphic equivalents in 1939, but other commitments during the war period necessitated deferment of completion of the project until the present time. The entire cost of the field expenses for the collection and the laboratory costs of the preparation of the mineral samples and of the chemical analyses was covered by grants from the Phillips Fund administered by the Department of Geology, Princeton University. Dr. H. L. James prepared the mineral concentrates for chemical analysis. All chemical analyses were made in the Laboratory for Rock Analysis at the University of Minnesota. Full details of the optical properties of the clinopyroxenes have been given by Hess (1949). A general account of the rocks of the Adirondack Mountains of Northern New York State has been previously published (Buddington, 1939).

## PYROXENES OF ANORTHOSITIC SERIES

All the pyroxenes (Table 1) from the rocks of the anorthositic series, with the exception of the most mafic (5) are richer in alumina (4 to 7%) and ferric iron oxide (2 to 3%) than those (2.3 to 3.5 per cent alumina and 0.6 to 1.5 per cent ferric iron) in normal gabbro, norite and diabase sheets. The anorthositic pyroxenes are also in general slightly higher in lime and markedly lower in magnesia. The implications would seem to be that the pyroxenes of the anorthositic series crystallized in a different environment, either in a chemically different magma, under different

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TABLE 1  
CLINOPYROXENES FROM ADIRONDACK ANORTHOSSITIC SERIES

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	FeO	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	TiO <sub>2</sub>	MnO	H <sub>2</sub> O+	H <sub>2</sub> O-	Other Con- stituents	Total
1	50.13	4.71	2.67	9.66	10.98	19.54	.81	.14	.58	.23	.91	.05		100.41
2	49.96	4.30	1.96	8.87	12.00	20.43	.52	.00	.67	.22	.64	.10		99.67
3	45.80	7.06	3.14	10.29	8.42	21.58	.68	.01	1.42	.20	.30	.10		99.00
4	46.85	5.03	2.91	13.63	7.03	21.90	.46	.00	1.47	.20	.24	.05		99.77
A	46.28	7.38	2.21	14.80	8.91	18.78	n.d.	n.d.	.59	n.d.	1.115			100.065
5	51.01	2.69	1.86	10.07	12.41	20.59	.47	.02	.40	.48	.19	.06		100.25
AVERAGE CLINOPYROXENE OF GABBRO AND NORITE FOR COMPARISON														
B	51.21	2.72	1.18	10.41	14.34	18.70	.29	.02	.73	.27	.16	.06	.09	100.18
C	50.39	3.95	1.73	9.20	15.15	17.82	.18	.09	.51	.19	.82		.07	100.10
ORTHOPIYROXENE														
6	51.21	2.14	1.02	25.89	17.15	1.59	.10	.06	.28	.51	.16	.08		100.19
D	50.33	3.36	1.03	19.40	21.40	2.77			.07	.71	1.14			100.21

physical conditions, or both. The nature of the differences would appear to be what might be thought to occur if the pyroxenes of the anorthositic series crystallized from a magma richer in the feldspathic constituents and poorer in magnesia than the normal gabbroic and noritic magmas. It was previously (Buddington, 1939, pp. 216–218, 235) concluded from field evidence that the anorthositic series was derived from a magma about equivalent to 85 per cent labradorite, 10 per cent pyroxene and five per cent of accessory minerals with a substantial quantity of volatiles. The hypothesis is therefore advanced here that the clinopyroxenes of the anorthositic series have a composition different from the clinopyroxenes of normal gabbroic and noritic rocks because they crystallized from a magma much richer in calcium and alumina and poorer in magnesia than the normal gabbroic and noritic magma.

## EXPLANATION OF TABLE 1

(1) Augite from coarse Marcy type of anorthosite, road cut SW end of outlet of Lake Clear, St. Regis quadrangle. Analysts, R. B. Ellestad and Lee C. Peck. Corresponds to analysis 22, p. 655, *Hess Am. Mineral*, 1949. From rock whose chemical analysis is given in *G. S. A. Mem.* 7, No. 7, opp. p. 24.

(2) Augite from anorthositic gabbro, Keene valley road, 1 mile WNW of intersection with main N-S highway, Elizabethtown quadrangle. Analyst, R. B. Ellestad. Corresponds to analysis 21, p. 655, *Hess Am. Mineral.*, 1949. From rock whose analysis is given in *G. S. A. Mem.* 7, No. 25, p. 36.

(3) Salite from gabbroic anorthosite gneiss, quarry 0.3 mile east of Stickney Bridge, Ausable quadrangle. Analyst, R. B. Ellestad. Corresponds to chemical analysis 24, p. 656, *Hess Am. Mineral.* 1949. From rock whose analysis is given in *G. S. A. Mem.* 7, No. 10, opp. p. 24.

(4) Ferrosalite from gabbro pegmatite in Marcy type of anorthosite, quarry 3 miles east of Wilmington on south shoulder of Hamlin Mt., Lake Placid Quadrangle. Analyst, R. B. Ellestad. Corresponds to chemical analysis 26, p. 657, *Hess Am. Mineral.*, 1949. From rock whose analysis is given in *G. S. A. Mem.* 7, No. 26, p. 36.

(A) Ferrosalite from coarse pegmatitic Marcy type anorthosite. A. B. Leeds, 1878.

(5) Augite from mafic gabbro dike. NE of schoolhouse, 2 miles SE of Gates Corners, Antwerp quadrangle. Analyst, Lee C. Peck. From rock whose analysis is given in *G. S. A. Mem.* 7, No. 47, p. 52.

(B) Average of 10 augites from the gabbroic, noritic and diabase sheets of Stillwater, Mont.; Bushveld, S. Africa; Triassic diabase of eastern U. S.; Duluth, Minn.; and Pigeon Point, Minn. Analyses 9–12 and 28–33 inclusive, *Hess, Am. Mineral.*, 1949.

(C) Average of 30 analyses of diallage pyroxene from the gabbro-norite family after P. Tschirwinsky, quoted in Schlossmacher K. Datensammlung gesteinsbildender Mineralien, 1931. *Fortschr. Min.* Bd. 19, T. 2, p. 253, 1935.

(6) Hypersthene from norite, a sharply defined layer in border facies of anorthosite, 1.7 miles W of Gabriels, Saranac Lake quadrangle. Analyst, Lee C. Peck. From rock whose analysis is given in *G. S. A. Mem.* 7, No. 24, p. 36. Sp. G. of hypersthene. = 3.543. Composition equivalent to diopside 5.8, enstatite 41.4 ferrosilite 46.5 ( $\text{En}_{17}\text{Fs}_{53}$ ).

(D) Hypersthene from coarse pegmatite, Marcy type. A. B. Leeds (1878). Composition equivalent to diopside 9.2, enstatite 49.6, ferrosilite 33.3 ( $\text{En}_{50}\text{Fs}_{40}$ ).

Very coarse pegmatite—like development of clinopyroxene is found locally in a facies of anorthosite with a little associated sulfide and apatite. Balk (1944) has referred such developments to the effect of volatiles. The coarse clinopyroxene he described has indices of refraction similar to that of the pyroxene (1) of the coarse Lake Clear anorthosite.

The clinopyroxene (ferrosalite, Table 1, No. 4) of a gabbro pegmatite vein with sharp crustification growth and sharp walls in anorthosite, however, is substantially richer in ferrous iron relative to magnesia than the clinopyroxene of other members of the anorthositic series. This is in the direction of change that might be expected of a late residual magmatic fraction. However, the plagioclase ( $An_{40-51}$ ) in the normal anorthosite and in the associated gabbro pegmatite ( $An_{48}$ ) veins do not show the difference in composition which might theoretically be expected in such a case. The pegmatitic local segregation facies however is reasonably explicable as crystallization from local volatile—rich facies of the magma.

The augite (5) is from a rock, consisting of about two thirds mafic constituents of which one half is augite, which occurs as a dike in anorthosite. The composition of the plagioclase is similar to that of the anorthosite and the composition of the augite is also similar to the composition of the pyroxene (1) of the coarse anorthosite but slightly richer in ferrous iron and lower in alumina and ferric iron and therewith similar to the augite of normal gabbro. It differs from augite of normal gabbro, however in a high lime content.

Our present experimental data and theoretical principles are either not adequate or have not yet been used in the right way to explain the correlation of some mineralogical and rock relationships of the anorthosite series.

The orthopyroxene (6) comes from a sharply defined layer of norite within anorthosite, and is a ferrosilite—rich member of the hypersthene group. This is appropriate for a late stage facies of the anorthositic series such as it seems to be though the plagioclase is similar to that of normal anorthosite. A coarse hypersthene from the anorthosite analyzed by Leeds (*D*) is more enstatic as is a coarse hypersthene ( $En_{79}Fs_{21}$ ) described by Balk (1944, p. 300).

#### PYROXENE AND GARNET IN METAMORPHIC CONTACT ZONES BETWEEN ANORTHOSITE AND MARBLE

There are numerous contact zones between anorthosite and included layers of marble in the Willsboro and adjacent part of the Ausable quadrangles. Usually there is a thin layered mafic gneiss with veined structure adjacent to the contact zone on the side of the anorthositic rocks and a skarn layer on the side next to the marble. The marble usually carries

disseminated silicates. The pyroxene disseminated in the marble may vary from diopside to ferrosalite and the garnet disseminated in marble from grossularite to an andraditic grossularite. Scapolite and wollastonite may also be present locally. Quartz is often an associate of the garnet. Sphene may be present as an accessory mineral.

A contact metamorphic zone between gabbroic anorthosite (Whiteface type) gneiss and marble near Willsboro has been previously described (Buddington, 1939, p. 41-42; and Broughton and Burnham, 1944).

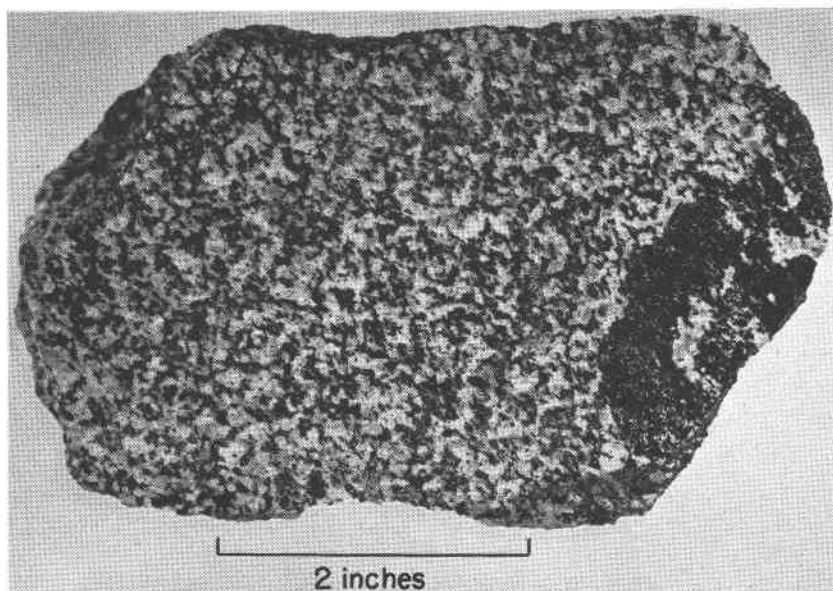


FIG. 1. Salite (near ferrosalite) gabbro, formed by assimilation of ferrosalite skarn (relic at right) in magma of gabbroic anorthosite composition. 3 miles SSW of Upper Jay, Lake Placid quadrangle.

Here the pyroxene from a skarn zone at contact with the anorthosite gneiss is a ferrosalite with the composition given in analysis 8. The high percentage of alumina is noteworthy.

At another locality, for about 3 miles SSW of Upper Jay on the Lake Placid quadrangle there is a synclinal sill of gabbro intruded into Grenville metasediments and containing random knots, shreds, and layers of ferrosalite skarn (Fig. 1). The bulk of the sill is more or less homogeneous but the rock has the appearance and texture of a member of the anorthositic series and its mafic character is attributed to disintegration of ferrosalite skarn with accompanying modification of the pyrox-

ene (Buddington, 1939, p. 39). The pyroxene of the gabbro (contaminated anorthosite) is a salite (No. 9) near ferrosalite in composition. The skarn pyroxene and the pyroxene of the contaminated anorthositic sill are similar to some of the pyroxenes of the normal anorthosite, particularly that (4) of the pegmatitic facies.

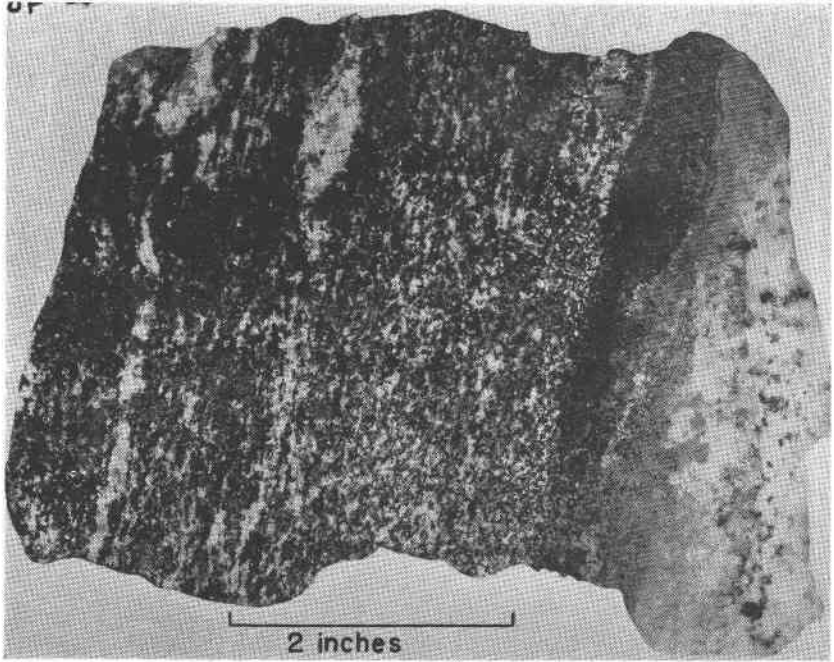


FIG. 2. Contact zone between gabbroic anorthosite gneiss and marble. Marble (light-colored) at right with disseminated andraditic-grossularite and ferrosalite. Mottled rock forming left 2/3rds of specimen is almandite-plagioclase-salite gneiss (mixed rock, mafic gneiss, formed from incorporation of ferrosalite skarn in gabbroic anorthosite). Narrow uniformly dark layer and thin light-gray layer between marble and gneiss is ferrosalite and andraditic grossularite skarn respectively. The two thin light-colored veinlets at left are younger granite pegmatite. Pokamoonshine quarry, Ausable quadrangle.

A contact zone between a mafic gneiss (a contaminated facies of the anorthosite) and an included layer of marble is well exposed on the floor of the old road material quarry near Pokamoonshine State Park, Ausable quadrangle. The marble layer is about 6 inches thick and carries disseminated ferrosalite (No. 7) and andraditic grossularite (No. 10). Between the marble and the mafic gneiss there is a narrow selvage consisting of andraditic grossularite skarn (No. 11) on the marble side and ferrosalite skarn next to the mafic gneiss. The mafic gneiss, about 2

feet thick, consists of plagioclase, salite (near ferrosalite) and almandite with a few thin granite pegmatite veinlets. (Fig. 2 is a photograph of a hand specimen from the contact zone). A short distance away there is a narrow layer of almandite-rich gneiss with subordinate plagioclase and pyroxene within the anorthosite which has the appearance as though

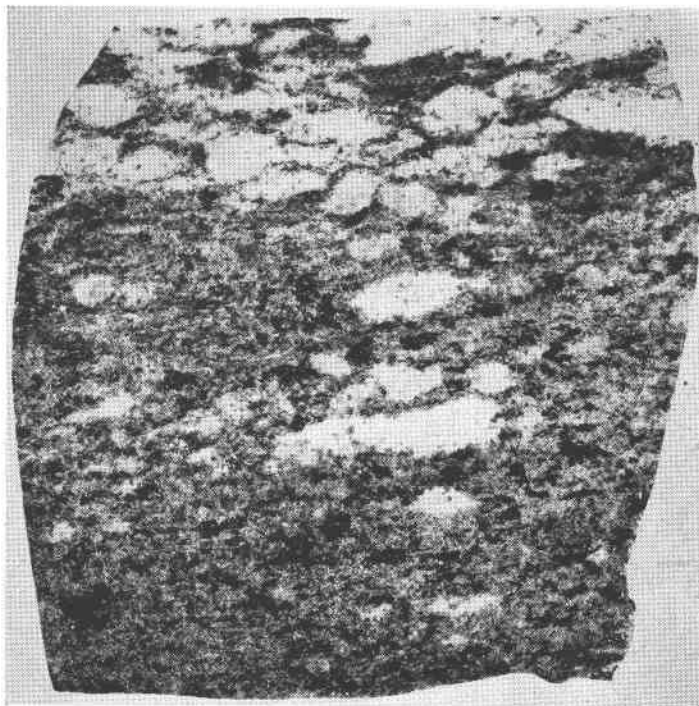


FIG. 3. Almandite-rich gneiss with subordinate pyroxene and plagioclase and augen of andesine. Andesine augen (white) are deformed porphyroblasts formed as replacement of ferrosalite skarn in contact zone between gabbroic anorthosite and marble. Almandite is later development, in part by reaction but in part with introduction of iron into mixed rock. Pokamoonshine quarry. Natural size.

pyroxene skarn were partly replaced by porphyroblastic plagioclase with subsequent development of almandite (Fig. 3). The garnet is an almandite (No. 12) and the plagioclase is oligoclase—andesine ( $Ab_{70}An_{30}$ ). Vein-like masses of almandite are also found locally to cross the foliation of the meta-anorthosite as replacement veins, selvages of almandite develop locally on the border of mafic-rich layers, and it seems probable that at least part of the development of almandite is subsequent to the development of a mixed rock of ferrosalite skarn and plagioclase with plagioclase porphyroblasts.

TABLE 2  
PYROXENES FROM CONTACT ZONE OF MARBLE AND ANORTHOSSITE

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	FeO	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	TiO <sub>2</sub>	MnO	H <sub>2</sub> O+	H <sub>2</sub> O-	S	Total
7	50.71	1.06	.53	18.57	5.70	22.86	.16	.02	.07	.18	.08	.04		99.98
8	45.30	7.74	3.36	12.27	7.04	21.74	.88	.16	1.30	.15	.39	.06		100.39
9	48.81	4.37	2.12	12.70	8.79	21.70	.53	.00	.70	.23	.10	.03		100.08

GARNETS FROM CONTACT ZONES BETWEEN ANORTHOSSITE AND MARBLE

10	38.57	18.88	5.22	2.27	.24	34.40	.00	.00	.34	.16	.04	.04	0.13	100.22*
11	38.57	17.54	6.76	3.00	.18	33.66	.00	.00	.42	.16	.05	.00		100.34
12	37.23	20.84	1.81	28.87	2.74	7.76	.00	.00	.17	.62	.08	.00		100.12
13	36.86	20.46	1.63	30.90	1.56	7.26	.09	.10	.16	1.13	.06	.04		100.25
14	37.30	21.04	1.01	29.29	2.77	7.37	.08	.06	.14	.93	.07	.03		100.09
15	37.23	20.91	1.40	28.37	2.13	9.01	.04	.02	.13	.92	.12	.04		100.32
16	37.48	21.01	1.12	27.25	3.48	8.45	.07	.03	.66	.82	.11	.05		100.53

\* Total=100.29

Less O for S = .07

Corrected total=100.22



Another contact zone between gabbroic anorthosite gneiss and marble is exposed along the railroad about 0.5 mile south of the tunnel east of Rattlesnake Mt., Willsboro quadrangle. Here too there is a mafic veined-gneiss facies, about 2 feet thick on the anorthositic side of the zone and a thin skarn layer on the marble side. The garnet of the mixed rock is an almandite (14).

A contact zone between gabbroic anorthosite gneiss and an included

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EXPLANATION OF TABLE 2

(7) Ferrosalite from dissemination in marble layer enclosed in Whiteface type anorthosite gneiss, Pokamoonshine quarry, Ausable quadrangle. Analyst, Lee C. Peck. Analysis No. 16, p. 652, Hess *Am. Mineral.*, 1949.

(8) Ferrosalite from feldspathic pyroxene skarn zone at contact with gabbroic anorthosite gneiss, 1.9 miles SW of Willsboro bridge, Willsboro quadrangle. Analysts, R. B. Ellestad and Lee C. Peck. Analysis No. 25, p. 657, Hess *Am. Mineral.*, 1949. From rock whose analysis is given in *G. S. A. Mem. No. 7*, No. 38, p. 44.

(9) Salite from gabbro, a facies of anorthosite mafic from incorporation of pyroxene skarn, quarry 2.5 miles SSW of Upper Jay, Lake Placid quadrangle. Analyst, R. B. Ellestad. Analysis No. 23, p. 656, Hess *Am. Mineral.*, 1949. From rock whose analysis is given in *G. S. A. Mem. No. 7*, No. 30, p. 36.

(10) Grossularite (andraditic) from dissemination in central part of a one-foot-thick marble layer enclosed in Whiteface type anorthosite gneiss, Pokamoonshine quarry, Ausable quadrangle. Analyst, Lee C. Peck. Sp.G.=3.652.

(11) Grossularite (andraditic) from massive garnet and pyroxene skarn layer at contact between mafic anorthosite gneiss and marble, same locality as 10. Analyst, Lee C. Peck. Sp.G.=3.670

(12) Almandite from gneissic feldspathic pyroxenic almandite layer several inches thick enclosed within Whiteface type anorthosite gneiss. Same locality as 10 and 11. Analyst, Lee C. Peck. Sp.G.=4.035. Plagioclase is oligoclase—andesine ( $Ab_{72}An_{28}$ ).

(13) Almandite from ultramafic pyroxene layer (? skarn) several feet thick enclosed within gabbroic anorthosite gneiss, road cut about 2 miles NW of Willsboro, Willsboro quadrangle. Analyst, Lee C. Peck.

(14) Almandite from a metamorphosed migmatite consisting of alternate laminae of pyroxene-garnet skarn and anorthosite, forming a 2-foot contact zone between anorthosite gneiss and marble,  $\frac{1}{2}$  mile south of R. R. tunnel east of Rattlesnake Mtn., Willsboro quadrangle. Migmatite has percentages of minerals as follows; plagioclase 28, almandite 26, potash feldspar 6, quartz 6, salite 12, hornblende 14, magnetite 6, and apatite 2. Analyst, Lee C. Peck.

(15) Almandite from metamorphosed migmatite of gabbroic anorthosite gneiss and schlieren and shreds of pyroxene-almandite skarn in contact zone between marble and anorthosite. The marble is a layer included within anorthosite. Locality is  $2\frac{1}{2}$  miles NE of Cross, Ausable quadrangle, road cut just south of intersection of side road and main highway. Migmatite has about the following percentages of minerals, andesine 60, microcline 5, quartz 0.5, almandite 18, pyroxene 8, hornblende 3, magnetite 4, and apatite 1.5. Some sphene is present. Chemical analysis of rock given in *G. S. A. Mem. 7*, Table 10, No. 40. opp. p. 44.

(16) Almandite from sparsely-disseminated porphyroblastic garnets in gabbroic meta-anorthosite gneiss, road cut just east of outlet of Long Pond, Willsboro quadrangle. Analyst, Lee C. Peck.

layer of marble has previously been described (Buddington 1939, No. 40, Table 10) from near Cross, Ausable, quadrangle. The mafic border facies of the anorthositic rock has the composition of a diorite and the structure of an arteritic migmatite comprised of anorthositic veinings or impregnations and skarn. Garnet forms about 18 per cent of the rock and is an almandite (No. 15).

The garnet from an ultramafic pyroxene layer within gabbroic anorthosite gneiss about 2 miles NW of Willsboro and a disseminated sparsely porphyroblastic garnet from gabbroic anorthosite in the same belt have been analyzed (Analyses 13 and 16). Both are almandite.

The clinopyroxene of the almandite-rich mixed rock of anorthosite veins and impregnations and pyroxene skarn in general is uniformly a salite with optical properties very similar to that of the salite (9) from the Jay gabbro (anorthosite contaminated by skarn) and represents a modification of the original skarn ferrosalites (7 and 8) whereby there is an increase in the ratio of magnesia to ferrous iron.

It was originally expected that the garnet concentrated on the anorthositic side of the contact with skarn would be found to have a direct genetic connection with the garnet of the skarn since both were related to the

TABLE 3. GARNET ANALYSES RECALCULATED TO EQUIVALENT MOLECULES

	Ratio Mol % MgO/FeO in Rock	Almandite	Pyrope	Grossularite	Andradite	Spessartite	
In Meta-limestone							
10		4.5	0.8	77.4	16.8	0.5	Pokamoonshine, Ausable quadrangle.
11		6.6	0.6	67.7	24.6	0.5	Pokamoonshine, Ausable quadrangle.
In Meta-anorthosite Veined Pyroxene Skarn Zone							
12		63.4	8.6	21.6	4.3	2.1	Almandite-rich layer in anorthosite-skarn migmatite, Pokamoonshine.
13		70.0	6.4	16.3	4.9	2.4	Corona garnet in pyroxene skarn, Willsboro.
14		66.3	11.2	17.4	2.9	2.1	Anorthosite-pyroxene skarn migmatite, Rattlesnake Mtn.
15	25/75	63.4	8.6	21.6	4.3	2.1	Anorthosite-skarn migmatite, Cross.
In Meta-anorthosite Gneiss							
15	22/78*	60.3	13.9	20.7	3.3	1.8	Porphyroblastic garnet, Long Pond, Willsboro.

\* Average of composite sample of similar rock.

contact zone. This has not proven to be the case. The garnet in the normal anorthositic gneiss and its local mafic contact facies has uniformly proven to be almandite, whereas the garnet in the skarn or disseminated in the marble equally uniformly belongs to the grossularite—andradite series. The concentration of almandite in such mixed rock is a local phenomenon and does not always occur in all mixtures of anorthosite-veined pyroxene skarn, though it is common.

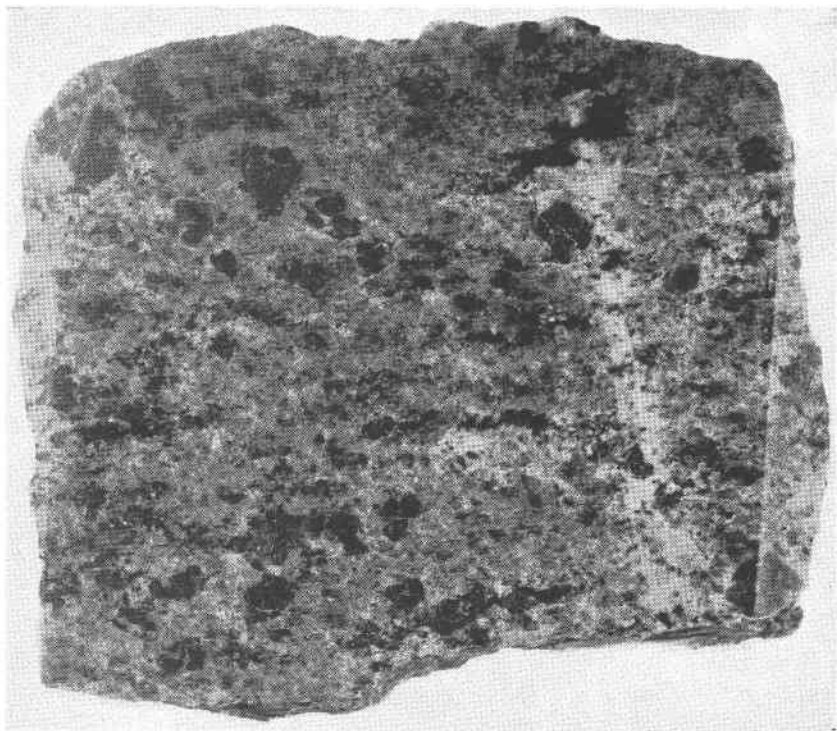


FIG. 4. Porphyroblastic almandite (large dark grains) in gabbroic anorthosite gneiss. Largely a regional metamorphic reaction product. East of outlet of Long Pond, Willsboro quadrangle.

It is believed that the following sequence of events will best serve to explain the minerals of the contact zones. (1) In the first stage of emplacement of a gabbroic anorthosite magma, disseminated diopside and ferrosalite developed consequent upon silication of the adjoining marble, and ferrosalite skarn formed adjacent to the magma itself; at least part of the grossularite-andradite may also have developed at this time; (2) the ferrosalite skarn was then intruded and impregnated

by anorthositic materials, somewhat modified in composition, and accompanied by porphyroblastic development of andesine in the skarn layer; (3) iron rich solutions especially affected the contact zones developing almandite in the mixed anorthosite—skarn rock and perhaps adding to the andradite-grossularite on the skarn and marble side. Periods 2 and 3 may well have overlapped; (4) the border zone of the great anorthosite massif as a whole together with its local mafic contaminated border facies was strongly deformed and underwent plastic flowage with the development of some corona almandite and the recrystallization and regrowth of porphyroblastic almandite. This was followed by injection of granite pegmatite veinlets and veins which in turn locally carry almandite.

Coronas of almandite at the contact between pyroxene and plagioclase are found in much of the feldspathic skarn and in migmatite and permeation mixed rock of skarn and anorthosite, so that the possibility may be considered that all the almandite has had an origin through reaction during regional metamorphism. Doubtless part of the garnet did have this origin. This would require substantial leaching of lime and silica together with some magnesia. The plagioclase of the very strongly garnetiferous rock is oligoclase-andesine ( $Ab_{70}An_{30}$ ) in contrast to the normal andesine-labradorite of the anorthosite, and consistent with this hypothesis. However, there is so much iron in the almanditic mixed rock that it would seem highly probable that some had been introduced. Local prehnitization of the plagioclase in the contact zones may be related to the movement of lime by hydrothermal solutions which effected the development of the almandite.

It seems equally probable however that the disseminated porphyroblastic garnet of the normal meta-anorthositic facies (Fig. 4) has developed from reaction between ferrosalite and plagioclase with but little modification in bulk chemical composition.

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