

THE ROLE OF YTTRIUM AND OTHER MINOR ELEMENTS IN THE GARNET GROUP¹

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ABSTRACT

Several minor and trace elements, notably yttrium, scandium and zinc, are very common in garnets. The frequent occurrence of several of these in particular varieties of garnet suggests isomorphism. Yttrium, heretofore considered to be a rare constituent of garnets, is very prevalent in spessartites. It has been found to occur in concentrations of greater than 2 per cent Y_2O_3 in a few manganese-rich garnets. The frequent association of yttrium and manganese in spessartites suggests that ions of Y^{+3} with an ionic radius of 1.06 Å have replaced ions of Mn^{+2} having an ionic radius of 0.91 Å, the radii being those of Goldschmidt. The substitution scheme is $Y^{+3}Al^{+3}$ for $Mn^{+2}Si^{+4}$. Scandium is most abundant in pyropes, and Sc^{+3} with an ionic radius of 0.83 Å may substitute for ions of divalent Mg (0.78 Å) or possibly for divalent Fe (0.83 Å) if enough almandite is present. Zinc is a common trace element in manganese, iron and magnesium-rich garnets and ions of divalent Zn (0.83 Å) may proxy for those of divalent iron. Other trace constituents detected in garnets include, Ga, Ti, Cr, Na, Li, Dy, Gd, Ho, Yb, Er, La, Ce, Nd, Pr, Sr, F, V, B, Be, Ge, Sn, Pb, Cu and Nb. Their hypothetical isomorphous relations to the major constituents are discussed. Included in the data are 7 new quantitative yttria determinations, visual spectroscopic analyses of more than 70 garnets, and spectrographic analyses of 2 yttria precipitates obtained from spessartites.

INTRODUCTION

The garnets form a well-defined group of minerals with respect to their essential chemistry, physical constants and geological environment. Ford (1915), Stockwell (1927), Winchell (1933), Menzer (1928), Fleischer (1937) and Levin (1949) have discussed the relationships between the chemical composition and the physical constants within the group. Heritsch (1926) and Wright (1938) have emphasized the unique association of the different garnets with particular geological environments. However, relatively little information has been published on the minor and trace element chemistry of the garnets. The present investigation was undertaken to determine (a) the prevalence of yttrium and other minor and trace elements in garnets; (b) the hypothetical isomorphous relationships, if any; and (c) the consequent relationships to the rock types in which they occur. The accessory constituents detected in garnets, during the present investigation, include: Y, Sc, Zn, Ga, Ti, Na, Li, Cr, Dy, Gd, Ho, Er, Yb, La, Ce, Nd, Pr, Sr, V, B, Ge, Be, Sn, Pb, Cu, F and Nb. Yttrium, heretofore considered to be a rare or uncommon

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TABLE 1. VISUAL SPECTROSCOPIC ANALYSES OF GARNETS
Determinations by H. W. Jaffe

<i>Key</i>																		
Major constituents	M															More than 5 per cent		
Minor constituents	m															0.5 to 5 per cent		
Trace constituents	t															Less than 0.5 per cent		
	—															Absent		
GROUP I—MANGANESE-RICH GARNETS																		
Sam- ple	Ca	Mg	Fe	Mn	Al	Si	Zn	Cr	Ti	Y	Sc	Li	Na	Sr	V	F	Ga	Nb
1.	t	m	M	M	M	M	t	—	t	t	—	—	t	—	—	—	t	—
2.	m	M	M	M	M	M	t	—	t	t	t	—	t	—	—	—	t	—
3.	t	t	M	M	M	M	t	—	t	m	t	t	—	—	t	t	t	—
4.	t	t	M	M	M	M	t	—	t	t	t	t	—	—	—	t	t	—
5.*	m	t	m	M	M	M	t	—	t	t	—	t	t	—	—	t	t	—
6.	m	m	M	M	M	M	t	—	t	m	t	—	t	—	—	—	t	—
7.	m	m	M	M	M	M	t	—	t	t	—	—	t	—	—	—	t	—
8.	m	t	M	M	M	M	t	t	t	t	t	t	t	—	—	—	t	—
9.	t	m	M	M	M	M	t	—	t	t	—	t	t	—	—	—	t	—
10.	t	m	M	M	M	M	t	—	t	t	—	—	—	—	—	—	t	—
11.	t	M	M	M	M	M	t	—	t	t	t	—	t	—	—	—	t	—
12.	m	t	M	M	M	M	t	—	t	m	t	t	t	—	—	—	t	—
13.	t	m	M	M	M	M	t	—	t	m	t	—	—	—	—	—	t	—
14.	m	t	M	M	M	M	t	—	t	m	t	t	t	—	—	—	t	—
15.	m	t	M	M	M	M	t	—	t	—	—	—	t	—	—	—	t	—
16.	t	m	M	M	M	M	t	—	t	t	—	t	t	—	—	—	t	—
17.	t	m	M	M	M	M	t	—	t	t	t	t	t	—	—	—	t	—
18.	t	t	M	M	M	M	t	—	t	t	t	t	t	—	—	—	t	—
19.	t	m	M	M	M	M	t	—	t	t	—	—	t	—	—	—	t	—
20.	m	m	M	M	M	M	t	—	t	t	—	—	t	—	—	—	t	—
21.	m	t	M	M	M	M	t	—	t	t	t	—	t	—	—	—	t	—
22.	t	m	M	M	M	M	t	—	t	t	t	—	t	—	—	—	t	—
23.	m	m	M	M	M	M	t	—	t	t	—	t	t	—	—	—	t	—
24.	t	M	M	M	M	M	t	—	t	t	—	t	t	—	—	—	t	—
25.	m	m	M	M	M	M	t	—	t	t	t	t	t	—	—	—	t	—
26.	t	t	M	M	M	M	t	—	t	t	—	t	t	—	—	t	t	—
27.	m	m	M	M	M	M	t	—	t	t	—	—	—	—	—	—	t	—
28.	m	m	M	M	M	M	t	—	t	t	—	—	t	—	—	—	t	—
29.	m	m	M	M	M	M	t	—	t	t	t	t	t	—	—	—	t	—
30.	m	m	M	M	M	M	t	t	m	t	t	t	t	—	—	—	t	—
31.	m	m	M	M	M	M	t	—	t	t	—	—	t	—	—	—	t	—
32.	m	m	M	M	M	M	t	—	t	t	t	—	t	—	—	—	t	—
33.	m	m	M	M	M	M	t	t	t	t	—	—	t	—	—	t	t	—
34.	m	m	M	M	M	M	t	—	t	t	t	t	t	—	—	—	t	—
35.	m	m	M	M	M	M	t	—	t	t	t	t	t	—	—	—	t	—
36.	t	t	M	M	M	M	t	—	t	t	—	t	—	—	—	—	t	—
37.	t	m	M	M	M	M	t	—	t	t	t	t	t	—	—	t	t	—
38.	m	m	M	M	M	M	t	—	t	t	—	t	—	—	—	—	t	—
39.	m	m	M	M	M	M	t	—	t	t	—	t	—	—	—	—	t	†
40.	t	m	M	M	M	M	t	—	—	m	t	—	—	—	—	—	t	—

Note: 2 garnets from pegmatite, Pala, Calif., also contained spectrographic traces of Ge, Sn, B and Zn, G. Steiger, U. S. Geol. Survey files.

Sam- ple	Ca	Mg	Fe	Mn	Al	Si	Zn	Cr	Ti	Y	Sc	Li	Na	Sr	V	F	Ga	Nb
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GROUP II—MAGNESIUM-RICH GARNETS

41.	m	M	M	m	M	M	t	—	t	t	—	t	—	—	—	—	—	—
42.	m	M	M	m	M	M	t	—	t	t	t	—	—	—	—	—	t	—
43.	m	M	M	m	M	M	t	—	t	t	t	—	t	—	t	—	—	—
44.	m	M	M	m	M	M	t	—	t	—	—	—	t	—	t	—	—	—
45.	m	M	M	m	M	M	t	—	t	—	t	—	t	—	—	—	—	—
46.	m	M	M	m	M	M	t	t	t	t	t	—	t	—	—	—	—	—
47.	m	M	M	m	M	M	t	—	t	t	t	—	—	—	—	—	t	—
48.	m	M	M	t	M	M	t	—	t	—	t	t	t	—	—	—	—	—
49.	m	M	M	t	M	M	t	—	t	—	t	—	t	—	—	—	—	—
50.	M	M	M	m	M	M	t	—	t	t	t	t	t	—	—	—	t	—
51.	m	m	M	m	M	M	t	—	t	t	—	—	—	—	—	—	—	—
52.	m	m	M	m	M	M	—	t	t	—	—	—	t	—	—	—	t	—
53.	M	M	M	m	M	M	—	t	t	—	t	—	—	—	—	—	t	—
54.	M	M	M	m	M	M	t	—	t	—	—	—	t	—	—	—	t	—
55.	m	M	M	m	M	M	—	—	t	—	—	—	—	—	—	—	—	—
56.	m	M	M	t	M	M	—	t	t	—	t	—	—	—	—	—	—	—
57.	t	M	M	m	M	M	—	t	m	t	—	—	t	—	—	—	—	—
58.	m	M	M	t	M	M	—	—	t	t	t	—	t	—	—	—	—	—
59.	m	M	M	m	M	M	t	t	t	t	t	t	t	—	t	—	t	—
60.	m	M	M	t	M	M	—	t	m	—	—	—	t	—	—	—	—	—
61.	m	M	M	m	M	M	t	t	t	t	t	—	t	—	—	—	t	—
62.	M	M	M	m	M	M	t	t	t	—	—	—	—	—	—	—	—	—
63.	m	M	M	m	M	M	t	t	t	—	t	—	—	—	—	—	—	—
64.	m	M	M	m	M	M	t	t	t	—	t	t	—	—	—	—	t	—
65.	t	M	M	m	M	M	t	t	t	t	t	—	—	—	—	—	t	—

GROUP III—CALCIUM-RICH GARNETS

66.	M	t	M	t	m	M	—	—	t	—	—	—	—	—	—	—	—	—
67.	M	t	M	m	m	M	t	—	t	—	—	—	t	—	—	—	t	—
68.	M	m	M	m	M	M	t	t	t	t	—	—	t	t	—	t	t	—
69.	M	t	M	m	M	M	t	—	t	—	—	—	t	—	—	—	—	—
70.	M	M	M	m	m	M	t	—	M	—	—	—	t	—	—	—	—	t
71.	M	t	m	t	M	M	t	t	t	—	—	—	t	t	—	—	t	—
72.	M	M	M	m	M	M	—	m	t	—	t	—	t	—	—	—	—	—
73.	M	m	M	m	t	M	—	—	t	—	—	—	t	—	—	—	—	—
74.	M	m	m	t	M	M	—	M	m	—	—	—	—	—	t	—	t	—
75.	M	m	m	m	M	M	—	t	t	—	—	—	t	—	—	t	—	—
76.	M	t	M	m	M	M	—	—	t	—	—	—	—	t	—	—	—	—
77.	M	t	M	m	M	M	t	—	t	—	—	—	—	—	—	—	—	—
78.	M	t	M	t	t	M	—	—	m	—	—	—	—	—	—	—	—	—

Note: Andradite, Beemerville, N. J., showed "Si, Al, Ca, Fe, Ti above 1%; Mg, Mn 0.X%; Y, Yb, Be 0.0X—0.00X%; Pb, Cu traces," spectrographic, A. T. Myers, U. S. Geol. Survey.

* + spectrographic traces of Sn and Ge, G. Steiger, U. S. Geol. Survey files.

† Cu, less than 0.5%.

INDEX TO TABLE 1

Locality	Occurrence	Refractive Index
1. Brown Derby mine, Gunnison County, Colo.	Pegmatite	$n=1.821$
2. Hackettstown, N. J.	Granite-gneiss	$n=1.820$
3. Wildomar, Calif.	Pegmatite	$n=1.820$
4. New Mexico	do	$n=1.805$
5. Amelia Courthouse, Va.	do	$n=1.803$
6. Brazil	do	$n=1.814$
7. Zionville, N. C.	do	$n=1.826$
8. Gotta Walden mine, Portland, Conn.	do	$n=1.812$
9. Bergdorff, Idaho	Heavy sand	$n=1.819$
10. Unaweep Canyon, Mesa Co., Colo.	Granite	—
11. Ober Creek, Alaska	Au placer	—
12. Gunnison Co., Colo.	Pegmatite	$n=1.820$
13. North Carolina	do	—
14. Kiarfvet, Sweden (U.S.N.M. C6780)	—	—
15. Broken Hill, New South Wales (U.S.N.M. R3437)	—	—
16. Haddam, Conn. (U.S.N.M. 4459)	Pegmatite	—
17. Raymond, Maine (U.S.N.M. 2756)	do	—
18. Ramona, Calif. (U.S.N.M. R3438)	do	—
19. Aschaffenburg, Bavaria (U.S.N.M. R3442)	—	—
20. Guilford Courthouse, Conn. (U.S.N.M. 96819)	Pegmatite	—
21. Nathrop, Colo. (U.S.N.M. 80457)	Rhyolite	$n=1.820$
22. Maine	Pegmatite	$n=1.810$
23. Montgomery County, Md.	do	—
24. Yancey County, N. C. (U.S.N.M. 80219)	do	—
25. Spruce Pine, N. C. (<i>U.S.G.S. Bull.</i> 878)	do	$n=1.808$
26. Moneta, Va. (<i>U.S.G.S. Bull.</i> 878)	do	$n=1.803$
27. Union Pt., Ga. (<i>U.S.G.S. Bull.</i> 878)	do	$n=1.803$
28. West Hawley, Mass. (<i>U.S.G.S. Bull.</i> 878)	do	$n=1.800$
29. West Cunningham, Mass. (<i>U.S.G.S. Bull.</i> 878)	do	—
30. King's Mt. Dist., S. C. (<i>U.S.G.S. Bull.</i> 878)	do	—
31. Bald Knob, N. C. (<i>U.S.G.S. Bull.</i> 878)	do	—
32. Gossan Lead, Va. (<i>U.S.G.S. Bull.</i> 878)	do	—
33. Macon County, Ga. (<i>U.S.G.S. Bull.</i> 878)	do	—
34. Geoffrey, S. C.	do	—
35. Shooting Creek, Va.	do	—
36. Striegen, Silesia (U.S.N.M. 7525)	—	—
37. New Mexico	Pegmatite	—
38. Fairfax Quad., Va.	—	—
39. North Carolina	Pegmatite	—
40. Do	do	—
41. Burlington, Vt.	Mica schist	—
42. Locality unknown	Chlorite schist	—
43. Avalanche Lake, Essex County, N. Y. (<i>Jour. Geol.</i> , 54, pp. 105-116, 1946)	Gabbro	$n=1.780$
44. Gore Mtn., N. Y.	Massive garnet	—

Locality	Occurrence	Refractive Index
45. Locality unknown	Granite-gneiss	—
46. McCall, Idaho	Heavy sand	—
47. Wyoming	Glaucophane schist	—
48. California	Mica schist	—
49. North Carolina	do	—
50. Chester, Vt.	do	—
51. St. Maries, Idaho	Placer	—
52. Burnsville, N. C.	—	—
53. Locality unknown	Mica schist	—
54. Do	Gneiss	—
55. Fort Wrangel, Alaska (<i>Am. Mineral.</i> , 12 , p. 343, 1927)	—	$n=1.807$
56. Hawk, N. C.	Schist	—
57. Lumpkin County, Ga.	—	—
58. New York, N. Y.	Manhattan schist	—
59. Meronitz, Czechoslovakia	Serpentine	—
60. Locality unknown	—	—
61. 5 miles NE of Dillard, Ga.	Biotite gneiss	—
62. Avery Quad., Idaho (U.S.N.M. 95679)	—	—
63. Mitchell County, N. C. (U.S.N.M. R3444)	—	—
64. New Mexico	—	—
65. Georgia	Schist	—
66. Essex County, N. Y.	Diopside, wollastonite tactite	—
67. Sierra Mts., Calif.	Tactite	—
68. West Adirondacks, N. Y.	Pyroxene skarn	—
69. Chula Vista, Calif.	Tactite	—
70. Colorado Springs, Colo.	—	—
71. Xalostoc, Mexico (<i>Am. Mineral.</i> , 12 , p. 343, 1927)	—	$n=1.742$
72. Santa Fe, Ariz. (Dana's System, p. 441)	—	—
73. Prince Rupert Island, B. C.	Tactite	—
74. So. California Desert (<i>Am. Mineral.</i> , 32 , p. 640, 1947)	Diopside, idocrase tactite	—
75. Democrat, N. C.	—	—
76. California	Tactite	—
77. Fairfield, Idaho	—	—
78. Sierras, Calif.	Tactite	—

element in garnet, is actually a very persistent trace or minor constituent of spessartite garnets where it may occur in concentrations of more than 2 per cent Y_2O_3 .

ANALYTICAL DATA

During the present investigation, more than 70 garnets were studied. All of these were subjected to visual spectroscopic analysis, using the equipment and methods described by Peterson, Kauffman, and Jaffe (1947), Gabriel, Jaffe and Peterson (1947) and Jaffe (1949). Major, minor, and trace constituents determined by this method and reported in this paper are defined as follows:

Major constituents (M)	More than 5%
Minor constituents (m)	0.5 to 5%
Trace constituents (t)	Less than 0.5%
Absent (-)	Less than 0.1% for those elements listed below.

The following elements have been detected in garnets in concentrations at least as low as 0.1% by means of visual spectroscopy:

Fe, Mn, Ca, Mg, Al, Cr, V, Ti, Sc, Y, Ga, Na, Li, Zn, Sr, Cb and F.

Yttrium, found to be a common trace constituent of spessartites, may be detected spectroscopically in concentrations lower than 0.01%.

TABLE 2. Y_2O_3 IN SPESSARTITE GARNETS

Sample (Numbers from Table 1)	Geological occurrence	% Y_2O_3
2. Hackettstown, N. J.	Granite-gneiss	0.29
3. Wildomar, Calif.	Pegmatite	2.48 (a)
4. New Mexico	do	.10
8. Portland, Conn.	do	.14
12. Gunnison County, Colo.	do	1.36 (b)
37. New Mexico	do	.26
Elk Mt., near Las Vegas, N. Mex.	do	2.01 (c)
Schreiberhau	No data	2.64 ("YO")
Iisaka, Japan	Pegmatite	2.45 ("Rare Earths")

Analyses 2, 3, 4, 8, 12 and 37 by A. M. Sherwood (new data).
 Analysis of Elk Mt., N. M. spessartite by Charles Milton (new data).
 Analysis of Schreiberhau spessartite by Websky (1868) as quoted in Dana's *System*.
 Analysis of Iisaka, Japan spessartite by Takeo Iimori (1938).
 (a) + spectrographic traces of (Sc, Gd, Dy, La, Ce, Nd, Pr) $_2O_3$.
 (b) + spectrographic traces of (Dy, Gd) $_2O_3$.
 (c) + spectrographic traces of (Yb, Dy, Er, Ho) $_2O_3$.

Quantitative Y_2O_3 determinations were made of 7 garnets, according to the method of Minami (1935). The sample is dissolved in concentrated hydrofluoric acid to remove the silica, and the residue is digested with very dilute hydrofluoric acid. The residue is dissolved and precipitated with strong potassium hydroxide solution, dissolved in hydrochloric acid and reprecipitated with ammonia. The precipitate is dissolved, the solution evaporated to a very small volume and the rare earths precipitated with oxalic acid. After standing for 12 to 24 hours the rare-earth oxalates are filtered off and ignited. For an evaluation of this method, the reader is referred to a paper by Sahama and Vähätalo (1939).

In addition to the visual spectroscopic and quantitative analytical determinations, spectrographic analysis was employed in two instances. Semiquantitative spectrographic analyses were made of two ignited oxalic acid residues obtained from spessartites in order to determine their purity as Y_2O_3 and to detect any additional rare earths that were coprecipitated. By this means of enrichment, traces of the Y earths, Dy and Gd, were detected in both instances. In one of the samples, traces of the Ce earths, La, Ce, Nd, and Pr, were also detected.

The visual spectroscopic analyses are given in Table 1, the quantitative analytical yttria determinations in Table 2, complete analyses of four yttrian garnets in Table 3 and the semiquantitative spectrographic determinations of two yttria precipitates in Table 4. The writer is indebted to Charles Milton of the U. S. Geological Survey for the unpublished complete analysis of the yttrian garnet from New Mexico given in Table 3.

RELATIONS BETWEEN THE COMPOSITION AND OCCURRENCE OF GARNETS

The unique relationships between the five major garnet molecules—spessartite, almandite, pyrope, grossularite, and andradite—and the rock types in which they occur have been noted by numerous investigators, particularly Wright (1938) and Heritsch (1926). Before considering any hypothetical isomorphism that may exist in the garnet group, a review of Wright's conclusions is necessary. Wright selected 223 garnets for which both complete quantitative analytical data and geological occurrence were given in the literature. The data are representative of a world-wide distribution of garnets composed essentially of the five major molecules. He converted the analytical values to spessartite, almandite, pyrope, grossularite, and andradite and showed that, with few exceptions, different combinations of the garnet molecules were associated with particular rocks. This is illustrated in Table 5.

TABLE 3. COMPLETE ANALYSES OF FOUR YTTRIAN SPSSARTITES

	Schreiberhau	Elk Mt., N. M.	Gunnison Co., Colo.	Iisaka, Japan
SiO ₂	35.83	34.99	36.84	34.95
Al ₂ O ₃	20.65	20.76	20.75	14.80
B ₂ O ₃	—	—	—	0.15
Fe ₂ O ₃	—	—	—	16.60
Y ₂ O ₃	2.64 ("YO")	2.01 (b)	1.36 (a)	2.45 ("R.E.")
MnO	8.92	29.60	16.80	22.28
FeO	31.52	10.76 (total Fe)	21.51	—
MgO	—	0.17	tr	—
CaO	0.76	1.17	1.95	4.52
BeO	—	—	—	0.39
Na ₂ O	—	—	tr.	1.67
K ₂ O	—	—	—	0.16
H ₂ O	—	0.75	0.76	0.45
CO ₂	—	—	—	0.41
Total	100.32	100.12	99.97	98.83

Schreiberhau, analyzed by Websky as quoted in Dana's *System of Mineralogy*, 6th ed., p. 442 (1892).

Elk Mt., N. M., analyzed by Charles Milton (new data).

Gunnison Co., Colo., analyzed by A. M. Sherwood (new data).

Iisaka, Japan, analyzed by Takeo Iimori, *Sci. Pap. Inst. Phy. Chem. Res., Tokyo*, No. 805, Vol. 34, p. 836 (1938).

(a) + spectroscopic traces of (Sc, Dy and Gd)₂O₃.

(b) + spectrographic traces of (Yb, Dy, Er, Ho)₂O₃.

It is significant to note that the pegmatite and granite garnets are essentially spessartite and almandite. Shand (1943), in a reference to garnets in eruptive rocks, also notes, "Garnet is sometimes prominent in aplite and pegmatite veins, and occasionally in acid lavas. The variety is almandine or spessartite." He notes further that the magnesian garnet, pyrope, is an unsaturated mineral and incompatible with quartz in eruptive rocks. Shand writes, "The magnesian garnet, pyrope, is restricted to very basic rocks such as peridotites, pyroxenites and serpentines, which are generally free from feldspar. There is nothing in the known facts of distribution of either melanite (andradite) or pyrope to suggest that these minerals are capable of forming in presence of an excess of silica." Pegmatite garnets were also investigated by Mosebach (1938), who determined that these garnets are all spessartite containing up to 40% almandite, some grossularite and occasionally pyrope. Five additional garnets analyzed by Milton (1937) are very representative of the pegmatitic-granitic environment. These show major amounts of spes-

sartite and almandite, trace to minor amounts of pyrope and grossularite and only trace amounts of andradite.

The results obtained by the author and given in Table 1 are in accord with those obtained by Heritsch (1926), Wright (1938) and Mosebach (1938) for pegmatite and granite garnets. Of the 40 garnets from pegmatitic-granitic rocks listed in Table 1, all contain major amounts of manganese and iron and only trace to minor amounts of magnesium and calcium. Inasmuch as no chemical analyses were made for Fe_2O_3 , it is not possible to state whether any appreciable amounts of andradite are present. All previous analytical data in the literature, however, indicate that andradite is the least abundant of the five major garnet molecules

TABLE 4. SPECTROGRAPHIC ANALYSES OF TWO Y_2O_3 PRECIPITATES FROM SPESSARTITES

Constituent	No. 12	No. 3
	Gunnison County, Colo., Per cent	Wildomar, Calif. Per cent
Y_2O_3	>10	>10
Sc_2O_3	—	.1 - .1
Pr_2O_3	—	.02 - .2
Nd_2O_3	—	.05 - .5
La_2O_3	—	.02 - .2
Ce_2O_3	—	.01 - .1
Dy_2O_3	.05 - .5	.08 - .8
Gd_2O_3	.005-.05	.005-.05

M. J. Peterson, spectrographer

NOTE: The yttria precipitate from the Elk Mt., N. Mex., spessartite (tables 2 and 3) was spectrographed by K. J. Murata who found Yb, Er, Dy and Ho to be present.*

* Fleischer, M., Private communication, 1949.

in garnets found in pegmatitic and granitic rocks. Wright concluded that "Spessartite and almandite constitute 85-90% of the molecules of garnets from pegmatites and granites. In general, if one of the major constituents is known, either spessartite or almandite, the other can be estimated within a reasonable error, with 5-15% left for the remaining molecules." From the data given in Table 1, it is evident that a correlation exists between manganese-rich garnets, pegmatitic environment and yttrium-enriched garnets. This will be elaborated further in the following sections of this report.

TRACE AND MINOR CONSTITUENTS OF GARNETS

That certain trace and minor elements are characteristic of particular varieties of garnet is not surprising in view of the associations of the

different garnets with particular rock types as proposed by Wright and Heritsch and verified during the present investigation. This affinity of particular accessory elements for the various garnets suggests isomorphism, which may be explained on the basis of similarities of ionic radii, using the values given by Goldschmidt (1929). The garnets studied during this investigation fall conveniently into three groups, categorized as follows:

Group	Diagnostic major elements	Association
I	Mn, Fe	Pegmatite, granite
II	Mg, Fe	Schist
III	Ca, Fe	Tactite

Although all garnets will not fit into one of the above groups, particularly a low-iron grossularite, a survey of the literature and the results of the present study suggest that the vast majority of garnets will fit this generalized grouping. While some schist garnets may contain major amounts of Mn and Ca, these elements are *not diagnostic*, as are Mg and

TABLE 5. AVERAGE PROPORTION OF FIVE MAJOR GARNET MOLECULES IN DIFFERENT ROCK TYPES (Adapted from Wright (1938))

Rock Types	Spes-sartite	Almandite	Pyrope	Grossu-larite	Andradite
Pegmatites	47.1	41.8			
Granites	36.0	56.8			
Garnets assoc. with contact action on siliceous rocks	30.7	56.4			
Biotite schists		73.0	13.8	6.0	
Amphibole schists		53.6	20.3	20.7	
Eclogites		18.5	37.4	39.1	
Kimberlites and peridotites		13.4	72.3	9.0	
Various basic rocks		34.4	20.7	28.7	15.6
Calcareous contact rocks				51.5	40.8

Fe, which will invariably be present in major amounts. Similarly, a pegmatite garnet will invariably contain major amounts of the diagnostic elements, Mn and Fe, and may in *unusual examples* also contain major amounts of Mg or Ca. There follows a discussion of the minor and trace elements characteristic of Groups I, II and III and their possible relationships to the major cations.

GROUP I. ACCESSORY ELEMENTS ASSOCIATED WITH GARNETS OF PEGMATITES AND GRANITES

Yttrium in garnets was reported as early as 1868 by Websky, as noted in Dana's *System of Mineralogy* (1892). Websky found 2.64% of

“YO” in a garnet that is listed under the almandites in Dana’s *System*. It is interesting to note, however, that the analysis (Table 3) shows major amounts of MnO. Magnesium and ferric iron are absent and calcium is only sparingly present. Dana also refers to another questionable yttrian garnet which yielded 6.6% of Y_2O_3 , but a second analysis showed only a trace of yttria. The “yttergarnets” mentioned by Dana are erroneously listed with the andradites. This is surprising, in view of the fact that the only yttrian garnet listed by Dana—the one analyzed by Websky—is clearly an almandite-spessartite. The only other analysis of an yttrian garnet published to date is that described by Iimori (1938). The garnet was found in a pegmatitic environment in Iisaka village, Fukushima Prefecture, Japan, where it is associated with feldspar, tengerite, yttrialite, fergusonite, thorogummite and xenotime. The garnet, which contains 2.45% of rare earths (Table 3), is referred to as a “spalmandine” by Iimori, although all of the iron is reported in the analysis as Fe_2O_3 . Calcium is present in minor amounts, and magnesium is absent. The garnet occurs as partly hollowed shells in which tengerite, the yttrium carbonate, is deposited. The rare earths found in the garnet are not listed, but the dominant earth in the intimately associated tengerite is yttrium. Minor amounts of Gd, Dy, and Er are reported as being next in abundance. It is unfortunate that Iimori did not identify the rare earths found in the garnet. The validity of this analysis will be discussed later.

Goldschmidt and Peters (1931) detected spectrographic traces of yttrium in several garnets but did not find more than trace amounts in any sample. The spectrographic values listed by these investigators also show that the largest traces of yttria occur in spessartites from plumasitic granite-pegmatite. These data are given in Table 6.

Sahama and Vähätalo (1939) also noted spectrographic traces of yttria in garnets. Sahama concludes “that an appreciable part of the yttrium earths in rocks remains outside the minerals orthite and monazite.”

Yttrium has also been noted in garnets by van der Lingen (1928). He detected this element in garnets but did not estimate the amounts present. It is interesting to note that this investigator detected the element by use of visual spectroscopy in the same manner as the author. Van der Lingen writes, “From a large series of observations the conclusion can be drawn that yttriferous garnets are not rare in South Africa. For this type of garnet, namely a spessartine containing yttrium, I propose the name emildine, the limitation being that the molecules of uvarovite must be absent, and that the molecule of pyrope is either wholly absent or only present as a trace.” For garnets containing a trace of yttrium associated with pyrope and uvarovite, he proposed the name, erinadine.

TABLE 6. SPECTROGRAPHIC TRACES OF YTTRIUM AND SCANDIUM IN GARNETS
REPORTED BY GOLDSCHMIDT AND PETERS (1931)

Sample	Geological occurrence	%Y ₂ O ₃	%Sc ₂ O ₃
Garnet, spessartite, Tveit, Norway	Granite-pegmatite	0.01	0.01
Garnet, spessartite, Sigdal, Norway	do	.01-.1	.0005
Garnet, mangan-grossularite, Arvold, Norway	—	.0001	—
Garnet, andradite, Kalkofen, Norway	—	< .0001	—
Garnet, almandite, Fort Wrangel, Alaska	—	< .0001	.0005
Garnet, Silberbach, Bavaria	Eclogite	.001	.01
Garnet, pyrope, Bohemia	do	< .001	.01
Garnet, Piedimonte, Italy	do	.001	.01
Garnet, Almeklovdalen, Norway	do	< .001	.01
Garnet, Tafjord, Norway	do	.001	.005
Garnet, Grytingvag, Norway	Eclogite-pegmatite	< .001	.001
Garnet, Kimberley, S. Africa	Kimberlite	< .001	.01

A further reference to yttrium in garnets was found in a paper by Björlykke (1937) on the granite pegmatites of southern Norway. Björlykke notes that, "The minerals which occur in both the magmatic and in the hydrothermal-pneumatolytic pegmatites generally are present in different habits, and with different compositions in the two types of occurrences. Spessartite and apatite of the cleavelandite-quartz pegmatites usually occur in ill-defined crystals intersected by blades of cleavelandite. They contain no detectable amount of Y-elements, while those of the magmatic pegmatites usually contain these elements in considerable amounts." He also states that spessartite occurs in the magmatic pegmatites "in euhedral crystals containing small amounts of Y-elements." In the hydrothermal-pneumatolytic pegmatites, spessartite occurs, "mostly in anhedral crystals without detectable amounts of Y-elements." His usage of the terms, "considerable amounts" and "small amounts" on two different pages is not clear. No percentages are given, and there is no indication, therefore, of the amounts present. It is noteworthy, however, that the yttrium detected by Björlykke is in manganese-rich garnets found in pegmatite. It is assumed that his "Y-elements" embrace the yttrium group: Y, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu.

The present writer found that yttrium is an especially common trace constituent of spessartite garnets. It was detected in 39 out of 40 spessartites studied (Table 1). It is less common in magnesium-rich garnets and uncommon in calcium-rich garnets (Table 1). In the course of the present investigation, seven quantitative yttria determinations were

made of spessartites, all associated with pegmatites. These are given in Table 2, along with the two analytical values of Websky and Iimori. Two new complete analyses of yttrian spessartites are given in Table 3 and are offered for comparison with those of Websky and Iimori. These represent the only four yttrian garnets that have been completely analyzed. The occurrence of the Japanese garnet has already been mentioned. The garnet from New Mexico, analyzed by Charles Milton, was submitted by V. Leon Guy of Las Vegas, New Mexico. It is reported to occur in pegmatite at Elk Mountain, northwest of Las Vegas. The garnet from Colorado, analyzed by A. M. Sherwood, was submitted by A. M. Crawford, Delta, Colo. Crawford states that it occurs "on the western slope in Gunnison County near Little Blue Creek, not far from the Black Canyon of the Gunnison River where there are a good many pegmatite dikes and feldspar deposits."

All four of the analyzed yttrian garnets (Table 3) are rich in manganese and ferrous iron and conversely impoverished in magnesium, calcium and ferric iron. Y^{+3} has an ionic radius of 1.06 Å and Mn^{+2} , an ionic radius of 0.91 Å. Divalent iron ions (0.83 Å) are too small to be expected to serve as hosts for the larger yttrium ions. Goldschmidt (1945) notes that the host mineral should have some main constituent with an ionic radius similar to the minor elements associated with it. This suggests that Y^{+3} may occupy Mn^{+2} positions in the garnet lattice due to similarities of ionic radii. Substitution of this type is not to be unexpected, according to Goldschmidt (1945), who writes, "Generally the possibility of large scale isomorphous substitution in minerals from magmas will be limited to such pairs of ions, the radii of which agree within a tolerance of 10–15 per cent of the larger radius of the pair. Divalent magnesium (0.78 Å) and ferrous iron (0.83 Å) freely replace each other in ionic crystals, but not magnesium and calcium (1.06 Å). Divalent manganese occupies a position intermediate between magnesium and calcium, having an ionic radius of 0.91 Å and entering into isomorphous substitution either for magnesium, or in many cases, for calcium. . . . Comparable to divalent calcium (1.06 Å) are—to a certain degree the divalent manganese (0.91 Å) . . . the trivalent ions of yttrium (1.06 Å) and all the trivalent lanthanide elements from lanthanum (1.22 Å) to lutecium (0.99 Å)."

Close inspection of the chemistry of the minerals associated with the yttrian spessartite from California (Tables 2 and 7) affords further illustration of the substitution of the yttrium for manganese. Table 7 includes visual spectroscopic analyses of all of the minerals present in the rock, a simple pegmatite, and Table 8, the ionic radii of the possible host and substitute ions. It is significant to note that the garnet is the only mineral of the assemblage that contains both yttrium (2.48% Y_2O_3)

and major amounts of manganese. Hence, it is reasonable to assume that all of the yttrium has entered the garnet lattice substituting for manganese on the basis of similarities of ionic radii. Scandium, on the other hand, is present in the muscovite and tourmaline as well as in the garnet (Table 7). Triply charged ions of scandium (0.83 Å) may proxy for divalent magnesium (0.78 Å) or iron (0.83 Å) according to Goldschmidt and Peters (1931), who state that trivalent scandium ions commonly proxy for either of these divalent ions. This is further emphasized by Sahama (1936). In the California garnet, muscovite and tourmaline (Table 7) scandium probably proxies for divalent iron as the pegmatite is impoverished in magnesium. Gallium is present in four of the five

TABLE 7. VISUAL SPECTROSCOPIC ANALYSES OF AN YTTRIAN SPESSARTITE AND ASSOCIATED MINERALS FROM A CALIFORNIA PEGMATITE
(Y_2O_3 in the spessartite = 2.48%)

	Ca	Al	Fe	Mn	Mg	Si	Y	Na	Li	K	Zn	Ti	V	Sc	Rb	Tl	Ga	B	F
Spessartite	t	M	M	M	t	M	m	—	t	—	t	t	t	—	—	t	—	t	—
Muscovite	t	M	m	t	t	M	—	m	t	M	—	t	t	t	t	t	t	—	t
Tourmaline	t	M	M	t	m	M	—	m	t	—	t	—	—	t	—	—	t	M	t
Albite	m	M	t	—	—	M	—	M	—	—	—	—	—	—	—	—	—	t	—
Quartz	—	—	t	—	—	M	—	—	—	—	—	—	—	—	—	—	—	—	—

Determinations by H. W. Jaffe.

minerals of the assemblage and this element may replace aluminum, the sizes of the respective trivalent radii being (0.62 Å) and (0.57 Å). Vanadium found in the garnet and the mica may supplant ions of aluminum as quadrivalent V (0.61 Å) ions. Titanium (0.64 Å) may similarly replace aluminum. Zinc (0.83 Å) present in the garnet and tourmaline may substitute for ferrous iron. Lithium (0.83 Å) found in the garnet, muscovite, and tourmaline may similarly proxy for divalent iron. Fluorine, found in the garnet, mica, and tourmaline should proxy for oxygen or hydroxyl.

To determine whether any additional rare earths were present in garnets, the yttria precipitates obtained from the California and the Colorado spessartites (Table 2) were subjected to spectrographic analysis. It was assumed that any additional rare earths present in the garnet would be coprecipitated with yttrium and therefore concentrated many fold. The results of these spectrographic analyses are given in Table 4. The ignited oxalic acid residues obtained from both garnets showed traces of the Y-elements gadolinium and dysprosium. These were not detected in the original visual spectroscopic analyses because of their low concentrations in the garnets. Traces of the Ce-elements—cerium, lanthanum, neodymium, and praseodymium—were also detected in the residue

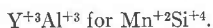
of the California garnet. According to Sahama,* the cerium earths had not been previously detected in garnets probably because enough material was not available for chemical enrichment. If all group precipitations, particularly those of the difficultly separable rare earths, were subjected to spectrographic analysis our geochemical knowledge would be greatly enriched.

TABLE 8. IONIC RADII IN ANGSTROMS (Goldschmidt 1929) AND SUGGESTED ISOMORPHISM

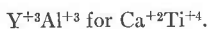
Ca ⁺²	Al ⁺³	Fe ⁺²	Mn ⁺²	Mg ⁺²	Si ⁺⁴	Y ⁺³	Na ⁺	Li ⁺	K ⁺	Zn ⁺²	Ti ⁺⁴	V ⁺⁴	Sc ⁺³	Rb ⁺	Tl ⁺	Ga ⁺³	B ⁺³	F ⁻	O ⁻²
1.06	0.57	0.83	0.91	0.78	0.39	1.06	0.98	0.83	1.33	0.83	0.64	0.61	0.83	1.49	1.49	0.62	0.20	1.33	1.32
Spessartite Mn(Y, Ca)	Fe(Zn, Sc, Mg, Li)		Al(Ga, V, Ti)		O(F)														
Muscovite	Fe(Mn, Mg, Sc, Li, Na)		Al(Ga, V, Ti)		O(F)		K(Rb, Tl)												
Tourmaline	Fe(Mn, Zn, Mg, Sc, Li, Na)		Al(Ga, Ti)		O(F)														
Albite																	Na(Ca)		

SUBSTITUTION OF YTTRIUM FOR MANGANESE

The substitution of ions of Y⁺³ for those of Mn⁺², as postulated, obviously upsets the neutrality of the crystal owing to higher positive charge of the former. This might be balanced, however, by a corresponding substitution of Al⁺³ ions for Si⁺⁴ ions in tetrahedral coordination. Al ions are known to proxy for Si ions in tetrahedral coordination in the amphiboles (Warren, 1929), micas (Jackson and West, 1930), clinopyroxenes (Hess, 1949) and in many other minerals. That Al may occupy Si positions in garnet has already been suggested by Alderman (1935). The substitution scheme in the yttrian spessartites might then be:



A similar substitution scheme involving yttrium is offered by Sahama (1946) in explanation of the sphene-keilhauite series. According to Sahama, the isomorphism is:



In the sphene lattice, however, the Al and Ti ions are believed to be in octahedral rather than tetrahedral coordination (Zachariasen 1930).

Based upon the suggested substitution of Y⁺³Al⁺³ for Mn⁺²Si⁺⁴, a theoretical yttrian spessartite containing 8.89% Y₂O₃ should be a stable garnet with the ideal composition calculated as shown at the top of the next page.

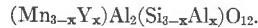
A garnet of this composition has recently been synthesized by H. S. Yoder at the Geophysical Laboratory. He has also been able to synthesize yttrian spessartites containing more than 8.89% yttria. Based upon

* Sahama, Th. G., Personal communication 1948.

Composition		Atomic Ratios		Cations to Twelve O	
SiO ₂	30.73	Si	512	Z=3	
Al ₂ O ₃	24.08	Al	472		
Y ₂ O ₃	8.89			80	592
MnO	36.30				
100.00		Y	80	X=3	
		Mn	512		
		O	2362		

Formula: $(Mn_{3-x}Y_x)Al_2(Si_{3-x}Al_x)O_{12}$, where $x=0.4$.

the substitution scheme suggested by the author, $Y^{+3}Al^{+3}$ for $Mn^{+2}Si^{+4}$. Dr. Yoder has suggested the following formula for yttrian spessartites:



The end members of the substitution series may then be expressed as:

1. $Mn_3Al_2Si_3O_{12}$ (spessartite).

2. $Y_3Al_2Al_3O_{12}$ (?).

or



The compositions of these calculated from the formulas, give:

	1	2
SiO ₂	36.40	—
Al ₂ O ₃	20.60	42.93
Y ₂ O ₃	—	57.07
MnO	43.00	—
	100.00	100.00

No yttrium aluminate of the composition of the end member is known to occur naturally. If it can be synthesized, in order for it to retain the garnet structure it would require the Al ions to be present in two coordinations. The garnet structure (orthosilicate) requires independent SiO₄ tetrahedra which are linked by AlO₆ octahedra. Therefore, an end member garnet of the composition, $Y_3Al_2Al_3O_{12}$, would require independent AlO₄ tetrahedra linked by AlO₆ octahedra with yttrium in the interstices, probably in eightfold coordination. Whether such a continuous substitution series is possible will soon be determined by Dr. Yoder's work on synthetic yttrian garnets.

The substitution of Y and Al ions for Mn and Si ions, respectively, should expand but not excessively distort the garnet lattice. The ionic radii of Y⁺³ (1.06 Å) and Al⁺³ (0.57 Å) are both larger than those they replace, Mn⁺² (0.91 Å) and Si⁺⁴ (0.39 Å). Menzer (1928) has shown that the large Ca ions (1.06 Å) in grossularite are surrounded by extremely

distorted oxygen polyhedra. Further, it is generally believed that in the titanian andradites, most and in some cases all of the Ti^{+4} ions (0.64 \AA) replace the much smaller Si^{+4} ions (0.39 \AA) expanding the unit cell (Zedlitz 1933 and 1935). A good example is the titanian andradite from Oberweisenthal quoted in Dana's *System* (analysis 32 under andradites). The atomic ratios indicate that most, if not all, of the Ti has replaced Si.

Composition		Atomic Ratios		Cations to Twelve O
SiO ₂	29.15	Si	483	Z = 3.11
TiO ₂	10.84	Ti	137	
		} 620		
Al ₂ O ₃	6.50	Al	127	Y = 2.01
Fe ₂ O ₃	21.92	Fe	274	
		} 401		
MgO	0.98	Mg	24	X = 2.75*
CaO	29.40	Ca	524	
		} 548		
98.79		O	2390	

* (The low value for X may be a reflection of the low summation and possibly the failure to determine FeO and MnO.)

Accordingly, if the Ti^{+4} ions (0.64 \AA) and the Ca ions (1.06 \AA) can occupy Z and X positions, respectively, in the garnets, and in large amounts, the lattice should be no more distorted by the acceptance of ions of Al^{+3} (0.57 \AA) and Y^{+3} (1.06 \AA). That 2.48% Y_2O_3 does not appreciably alter the spessartite lattice is shown by the x-ray data in Table 9. The differences in spacings shown in these patterns are due essentially to the relative amounts of almandite and spessartite present rather than the small amount of yttria. In any event, the amount of expansion of the lattices of garnets containing small amounts of yttrium would be hidden by the much more important variable, the ratio of almandite to spessartite. That yttrian spessartites have a larger lattice than pure spessartite (never found in nature) will be illustrated by Dr. Yoder in his report on synthetic yttrian spessarittes. The garnet lattice, then, like that of the micas, appears to be quite elastic and capable of housing ions of a wide range of size in large amounts.

To date, only four naturally occurring yttrian garnets have been completely analyzed (Table 3). Calculating the atomic ratios of the yttrian garnets from Schreiberhau, Elk Mt., N. Mex., and Gunnison County, Colo. (Table 3), on the basis of $Y^{+3}Al^{+3}$ proxying for $Mn^{+2}Si^{+4}$, the following ratios are obtained (Table 10).

The fourth analysis of an yttrian garnet from Iisaka, Japan (Table 3), is questionable, as the atomic ratios for garnet cannot be satisfactorily calculated. The analyst, Iimori (1938), refers to the garnet as a "spal-

TABLE 9. X-RAY DIFFRACTION PATTERNS OF SPESSARTITES

3 <i>d</i>	4 <i>d</i>	5 <i>d</i>	8 <i>d</i>	16 <i>d</i>	<i>hkl</i>	<i>I</i>
2.90	2.91	2.92	2.92	2.90	400	m
2.60	2.60	2.61	2.61	2.60	420	vs
2.48	2.48	2.49	2.49	2.48	332	w
2.37	2.37	2.38	2.38	2.38	422	w
2.28	2.29	2.29	2.29	2.28	510	w
2.12	2.13	2.13	2.13	2.12	521	m
2.07	2.06	2.06	2.07	2.06	440	w
1.888	1.890	1.895	1.890	1.884	611	s
1.734	—	—	—	—	622	w
1.678	1.680	1.686	1.684	1.678	444	s
1.613	1.615	1.618	1.615	1.613	640	m
1.556	1.558	1.558	1.558	1.554	642	s
1.492	1.488	—	—	—	—	w
1.453	1.457	1.455	1.461	1.457	800	w
1.301	1.304	1.305	1.305	1.301	840	w
1.269	1.272	1.272	1.274	1.268	842	m

% Y₂O₃

#3—Wildomar, Calif.

2.48

#4—New Mexico

0.10

#5—Amelia Courthouse, Va.

tr.

#8—Gotta Walden mine, Portland, Conn.

tr.

#16—Haddam, Conn.

tr.

vs—very strong

s—strong

m—medium

w—weak

Determinations by G. E. Ashby.

mandine” and paradoxically reports all of his iron as Fe₂O₃. All attempts to calculate the atomic ratios of this garnet have been unsatisfactory, whether the iron is calculated entirely as Fe₂O₃ or as FeO. The presence of 1.67% Na₂O and some CO₂ and K₂O is not clear, and the sample may not have been pure. The best ratios are obtained by assuming that both ferrous and ferric iron are present and that Na⁺¹Y⁺³ replaces 2Mn⁺². Recasting the analysis on this basis the ratios may be as shown at the top of the next page.

In view of the questionable validity of this analysis, the unwarranted recasting of the iron, and the assumptions regarding the various substitutions, the isomorphism of Na⁺¹Y⁺³ for 2Mn⁺² in spessartites is purely speculative. However, in fairness to Iimori, who made a very detailed examination of the associated tengerite, his analysis of the yttrian garnet

Reported Composition		Fe recasted	Atomic Ratios		Cations to Twelve O
SiO ₂	34.95		Si	582 582	Z=2.98
Al ₂ O ₃	14.80		Al	290	Y=2.06
B ₂ O ₃	0.15		B	4	
BeO	0.39		Be	16	
Fe ₂ O ₃	16.60	7.30	Fe ⁺³	91	
FeO	—	9.30	Fe ⁺²	129	
Y ₂ O ₃	2.45 ("R.E.")		Y	22	
MnO	22.28		Mn	314 600	X=3.08
MgO	—		Ca	81	
CaO	4.52		Na	54	
Na ₂ O	1.67				
K ₂ O	0.16		O	2341	
H ₂ O	0.45				
CO ₂	0.41				
98.83					
n=1.830		(If Na ⁺¹ Y ⁺³ replaces 2Mn ⁺² there remains an excess of Na			
G=4.21		ions.)			

should not be discredited until such time as we have more data regarding the role of the various minor constituents in garnets. Although the garnets have been studied by numerous investigators, there are several aspects of their constitution that have not been sufficiently clarified. For example, Fermor's work (1926) on some Indian garnets, suggesting the presence of Mn₂O₃, has been regarded with some skepticism, perhaps unjustly so. Unless the presence of trivalent manganese is assumed satisfactory atomic ratios cannot be calculated for the garnet from Chargoon, India (Fermor 1926), one from Amelia, Va. (Dana 1892 and Shannon 1927), and another from Nathrop, Colo. (Dana 1892). Similarly, the role of titanium in garnets has not been well defined. Apparently it plays a dual role, proxying both for silicon in the Z group and aluminum in the Y group. The answers to these and other problems pertaining to the chemistry of the garnets can best be obtained by synthesizing the various garnets and their possible analogues.

GROUP II. ACCESSORY ELEMENTS ASSOCIATED WITH GARNETS OF SCHISTS

As previously stated, this group usually contains major amounts of magnesium and iron and may also contain appreciable amounts of calcium and to a lesser extent manganese.

Scandium is a very characteristic trace element in the pyrope-rich garnets of this group. In all probability, it substitutes for magnesium and possibly for divalent iron. Goldschmidt and Peters (1931) note that

TABLE 10. ATOMIC RATIOS OF ANALYZED YTTRIAN GARNETS CALCULATED ACCORDING TO SUBSTITUTION, $Y^{+3}Al^{+3}$ FOR $Mn^{+2}Si^{+4}$

Composition		Atomic Ratios*		Cations to Twelve O
<i>Schreiberhau</i>				
SiO ₂	35.83	Si	597	Z = 3.08
Al ₂ O ₃	20.65		23	
Fe ₂ O ₃	—	Al		405
Y ₂ O ₃	2.64		382	
MnO	8.92	Fe ⁺³		—
FeO	31.52			
MgO	—			
CaO	0.76	Y	23	X = 2.99
H ₂ O	—	Mn	126	
		Fe	439	
	100.32	Mg	—	
		Ca	14	
O 2414				
<i>Elk Mt., New Mexico</i>				
SiO ₂	34.99	Si	583	Z = 3.01
Al ₂ O ₃	20.76		18	
Fe ₂ O ₃	—	Al		407
Y ₂ O ₃	2.01		389	
MnO	29.60	Fe ⁺³		—
FeO	10.76			
MgO	0.17	Y	18	X = 3.05
CaO	1.17	Mn	417	
H ₂ O	0.75	Fe	150	
		Mg	4	
	100.12	Ca	21	
O 2395				
<i>Gunnison County, Colorado</i>				
SiO ₂	36.84	Si	613	Z = 3.09
Al ₂ O ₃	20.75		12	
Fe ₂ O ₃	—	Al		407
Y ₂ O ₃	1.36		395	
MnO	16.80	Fe ⁺³		—
FeO	21.51			
MgO	tr	Y	12	X = 2.88
CaO	1.95	Mn	237	
Na ₂ O	tr	Fe	299	
H ₂ O	0.76	Mg	—	
		Ca	35	
	99.97	Na	—	
O 2426				

* In calculating the atomic ratios, all of the yttrium must be placed in the X group of cations. When this is done, a corresponding amount of aluminum must be removed from the Y group and added to the Z group in order to achieve crystal neutrality. Thus, the substitution is $Y^{+3}Al^{+3}$ for $Mn^{+2}Si^{+4}$.

scandium follows magnesium and ferrous iron and concentrates in the ultrabasic rocks in garnet, olivine, and augite. Sahama (1936) also notes that scandium is abundant in several Finnish garnetiferous peridotites. The author found traces of scandium in 18 out of 26 garnets of this group (Table 1). Zinc was detected in 18 of these garnets and may proxy for ferrous iron as suggested in the previous group. Chromium was observed in 10 of these garnets and may replace aluminum, the respective trivalent ionic radii being 0.64 Å and 0.57 Å. Faint traces of yttrium were detected in 12 of these garnets. In this group, it may proxy for either calcium or manganese, the former, however, is generally more abundant. There are no instances where yttrium becomes more than a trace constituent of the garnets of schists. Yttrium, then, is the most characteristic trace constituent of the pegmatite garnets whereas scandium may occur in both pegmatite and schist garnets, but is more at home in the latter environment.

GROUP III. ACCESSORY ELEMENTS ASSOCIATED WITH GARNETS OF TACTITES

This group invariably contains major amounts of calcium and iron and may also contain appreciable amounts of chromium. Schorlomite, the titanium-rich garnet also belongs here. Calcareous contact metamorphic rocks or tactites are the type environment for this group. Wright (1938) notes that grossularite and andradite represent over 90% of the garnet molecules in these rocks and that it is possible to estimate the composition by determining the index of refraction alone. It is interesting to note that manganese was detected in all of the garnets of this group in small amounts (Table 1). The author has not found any variety of garnet that is entirely free of manganese.

Chromium and titanium are the most characteristic accessory elements found in this group and may produce the less common uvarovites and schorlomites. Strontium was observed in a few of the garnets of this group and may replace calcium, the respective radii being 1.27 Å and 1.06 Å.

One sample, a schorlomite from Colorado, contained a trace of niobium. Pentavalent Nb has an ionic radius of 0.69 Å and should proxy for quadrivalent Ti possessing a radius of 0.64 Å. Inasmuch as only one true schorlomite was studied, the prevalence of niobium in schorlomites is not significant. However, the presence of this element in garnet has been noted by Rankama (1949) who has emphasized the affinity of niobium for titanium minerals.

CONCLUSIONS

1. A survey of the literature plus independent visual spectroscopic analyses of more than 70 garnets reaffirms Wright's study of the associations of certain garnets with particular rock types.

2. Yttrian garnets are not as rare as previously suspected and are characteristically associated with pegmatites. They are not to be classed with the andradites as indicated by Dana but rather with the spessartites.

3. Yttrium occurs in some pegmatite garnets in concentrations of greater than 2% Y_2O_3 where it may proxy for manganese. The substitution appears to be $Y^{+3}Al^{+3}$ for $Mn^{+2}Si^{+4}$.

4. Traces of the other rare earths, particularly Dy, Gd, and to a lesser extent Ho, Er, Yb, Ce, La, Nd, and Pr, not previously detected in garnets were found in spessartite.

5. Scandium is a characteristic trace constituent of the magnesium and iron rich schist garnets and to a lesser extent of pegmatite garnets.

6. Traces of Ga, Ti, Li, Na, F, Zn, Cr, Sr, Nb, V, Be, B, Ge, Sn, Pb and Cu are present in garnets.

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