

## GROSSULAR-SPESSARTINE-ALMANDINE GARNETS FROM SOME JAPANESE SCHEELITE SKARNS

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### ABSTRACT

Garnets from the Kuga, Fujigatani and Kagata mines, typical scheelite skarn deposits in Japan, are found with the electron probe to be close to grossular in composition with more or less substitution of Mn and Fe<sup>2+</sup> for Ca. Compositional zoning observed in some euhedral to subhedral crystals consists of a gradual increase in the Mn and Fe<sup>2+</sup> contents from core to rim. The compositional variation of garnets, given by Brown (1969), Ackermann *et al.* (1972) and the present study, confirms the formation of solid solution among grossular, spessartine and almandine, even under conditions of relatively low temperature and pressure.

### SOMMAIRE

Les grenats provenant des mines Kuga, Fujigatani et Kagata, gîtes typiques de skarn à scheelite, s'avèrent, à la microsonde, proches d'un grossulaire dont les atomes de Ca sont partiellement remplacés par des atomes de Mn et de Fe<sup>2+</sup>. Les zones de composition observées dans certains cristaux idiomorphes-à-hypidiomorphes traduisent l'accroissement de la teneur en Mn et en Fe<sup>2+</sup>, du centre vers la périphérie. La variation dans la composition des grenats, observée par Brown (1969), par Ackermann *et al.* (1972) et dans le présent travail, confirme la formation de solutions solides entre grossulaire, spessartine et almandin, même à température et pression relativement basses.

(Traduit par la Rédaction)

### INTRODUCTION

It is well known that garnet forms solid solution series with various end members, among which the following five are common: pyrope, almandine, spessartine, grossular and andradite. The first three are called the pyralspite series and the last two, the grandite series. Although continuous solid solution seemed to be absent (e.g. Deer *et al.* 1962), recent studies of synthetic and natural garnets in the two series are revealing that various degrees of solid solution are possible, depending on the conditions of formation.

Microprobe analyses of grossulars from scheelite-bearing skarn deposits in Japan, indi-

cate that the garnets form a continuous solid solution which extends from grossular to spessartine-almandine. In this paper occurrences and analyses of these garnets will be described.

The recent development of techniques for high-temperature and high-pressure experiments has allowed syntheses of a wide range of garnet solid solutions. One of the problems at present in garnet mineralogy is the determination of the dependence of the solid solubility among garnet end members and the conditions of formation. The present paper will demonstrate that nearly complete solid solution is possible among almandine, spessartine and grossular even under relatively low-temperature and low-pressure conditions.

### PREVIOUS WORK

Complete solid solution between pyrope and almandine, almandine and spessartine, and grossular and andradite is well-established. However, some conventional wet-chemical analyses have given "unusual" compositions, such as those rich in both Mn and Ca, or rich in Fe<sup>2+</sup> and Ca (see Tröger 1959 and Němec 1967). Although these garnets were reported as single phases having characteristic refractive indices and/or unit-cell constants, it was not considered in most papers that the garnets might exhibit compositional zoning or heterogeneity that could not be distinguished with wet-chemical techniques. With the development of the electron probe, it has become possible to study in detail the compositional variation and zoning of garnets. Brown's (1969) paper, on zoned garnets from quartzo-feldspathic schists of several greenschist-facies terrains in the world, could be cited as an example of such detailed study of compositional variation.

Brown's (1969) results cover a wide area in the almandine-spessartine-grossular diagram as shown in Figure 1. The Figure also includes the microprobe-determined compositional range of almandine-grossular garnets from low-grade metamorphic rocks of the Tauern area, Austria (Ackermann *et al.* 1972). The results indicate that almandine-spessartine garnets can incor-

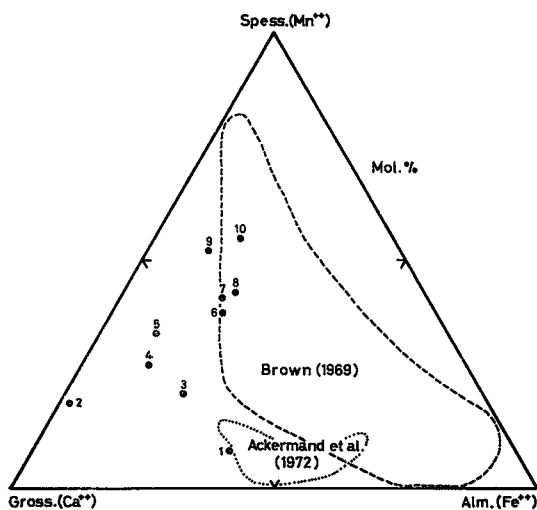


FIG. 1. Plot of some garnets with intermediate compositions between the almandine-spessartine join and grossular. Dashed line and dotted line represent microprobe compositional ranges of garnets from several greenschist-facies terrains (Brown 1969) and from low-grade metamorphic rocks of the Tauern area, Austria (Ackermänd *et al.* 1972), respectively. 1: regionally metamorphosed garnet skarn, Kadov, Moravia (Němec 1967). 2: Franklin, New Jersey (Fronde! & Ito 1965). 3: regionally metamorphosed Mn-rich sediment, Bastjörn, Sweden (Magnusson 1940). 4-5: sheared parts of granodiorite, Victory mine, Nevada (Lee 1962)\*. 6: quartzose pelitic schist, Katsuyama, southwestern Japan (Hashimoto 1968). 7: K-feldspar-garnet-apatite rock, Kotakarra, India (Fermor 1934)\*\*. 8: quartz-wolframite vein, Kaneuchi mine, central Japan (Ashida & Onuki 1963). 9: Mn deposit, Guettara, Algeria (Byramjee & Meindre 1956). 10: garnet-quartz rock, Sakrasanhalli, India (Fermor 1934)\*\*.

\*According to unit-cell dimension data, "Garnet A" by Lee (1962) seems to be a mixture. It is omitted in the present plot.

\*\*Data for these two garnets from India are from Tröger (1959) and Lee (1962).

porate considerable amounts of Ca under metamorphic conditions of greenschist to low-temperature amphibolite facies.

In the literature most garnets reported to have intermediate compositions between the almandine-spessartine join and grossular are close to, or included in, the ranges given by Brown (1969) and Ackermänd *et al.* (1972). Published results of wet-chemical analyses of some garnets which are close in composition to those studied in the present paper are plotted in Figure 1. Natural occurrences of continuous solid solution be-

tween the grossular corner and the analyses of Brown and Ackermänd *et al.* in Figure 1 have not yet been confirmed, to the present writer's knowledge, by electron probe microanalysis.

#### OCCURRENCE OF GROSSULAR-SPESSARTINE-ALMANDINE GARNETS

One of the characteristic features of scheelite-bearing skarn deposits in Japan is that the main constituent minerals are generally poor in ferric iron (Shimazaki 1974). In accordance with this fact, garnets from the skarns are poor in  $Fe^{3+}$ , and rich in Al. The Kuga, Fujigatani and Kagata mines are typical scheelite skarns in limestone, and have genetic relations to granitic intrusions. The grossular garnets in these deposits were found to contain considerable amounts of Mn and  $Fe^{2+}$ . The following is a brief description of the occurrence of these garnets.

*The Kuga mine* is a tungsten-copper deposit 30 km southwest of Hiroshima City, southwestern Japan. The area consists of Upper Palaeozoic to Lower Mesozoic formations of slate, sandstone, chert and limestone intruded by Late Cretaceous granitic rocks. According to Imai & Ito (1959), the main constituents of the Kuga deposits include andradite, Ca-clinopyroxene, wollastonite, epidote, actinolite, quartz, scheelite, cassiterite, chalcopyrite, pyrrhotite, arsenopyrite and pyrite.

Although Imai & Ito (1959) recognized andradite as one of the main skarn minerals, all garnets from the deposits studied by the present writer are grossular with more or less Mn and  $Fe^{2+}$ . As there are many ore deposits in this mine, and the samples studied were randomly collected from several, the occurrence of grossular garnets with Mn and  $Fe^{2+}$  could be regarded as a common feature. Under the microscope, the garnets often show distinct zoning with anomalous anisotropism. Clinopyroxenes associated with garnet are hedenbergites with considerable amounts of Mn.

*The Fujigatani mine* is 5 km southeast of the Kuga mine, and has a similar geological setting. The main constituents of the deposits are hedenbergite, grossular, plagioclase, wollastonite, vesuvianite, amphibole, quartz, calcite, fluorite, chlorite, sericite, stilpnomelane, scheelite, pyrrhotite, chalcopyrite, arsenopyrite, sphalerite, galena and so on (Ito 1962; Sato 1975, and the present study). Based on unit-cell size and refractive index, Ito (1962) suggested that garnets are generally grossular with 5 to 20 mol. %  $Fe^{3+}$ . In the present study, garnets collected from the Akemidani deposit (the main deposit in this

mine) are confirmed to be close to grossular, and some have considerable amounts of  $\text{Fe}^{2+}$  and Mn, especially at the margins of euhedral grains. Under the microscope, the garnets are generally distinctly to weakly anisotropic.

The Kagata mine is about 90 km north-north-east of Tokyo. The area consists of Late Palaeozoic shale, sandstone, chert and thin lenses of limestone intruded by a Late Cretaceous biotite granite. Although the mine was closed about 20 years ago, specimens were collected from old dumps. The main constituent minerals include garnet, Ca-clinopyroxene, wollastonite, a  $\text{Ca}_3\text{Fe}^{2+}\text{Si}_6\text{O}_{18}$  phase with the bustamite structure (so-called iron-wollastonite), actinolite, scheelite, pyrrhotite, pyrite and chalcopyrite (Shimazaki & Yamanaka 1973). Garnets from this mine are generally close to grossular in composition, and show very weak anisotropism under the microscope. In some specimens,  $\text{Fe}^{2+}$  and Mn-rich portions of the garnets have a compositional heterogeneity or zoning.

#### ANALYTICAL PROCEDURE AND RESULTS

About 30 polished- and polished thin-sections of skarns from the Kuga, Fujigatani and Kagata mines were prepared for electron probe analyses

of the garnets. Count-ratios of the sample to the standard were measured for Si, Al, Fe, Mn, Mg and Ca. The ratios were converted into oxide weight percentages using the method of Bence & Albee (1968). Detailed descriptions of the analytical procedure and the correction factors used in this study have been given by Nakamura & Kushiro (1970). In the present study, the totals of the corrected weight percentages of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{FeO}$ ,  $\text{MnO}$ ,  $\text{MgO}$  and  $\text{CaO}$ , are usually in the ranges of 98.5 to 101.5%.

Ratios of ferric and ferrous iron are important to determine the composition of garnets. Numbers of cations including  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  are calculated to satisfy the following two conditions: (1) total number of oxygens is 12.00, and (2) some Fe is taken as ferric to fill the six-coordinated position so that  $\text{Al} + \text{Fe}^{3+} = 2.00$ . The remainder of the Fe is assumed to be ferrous (see Table 1). After these calculations, molecular percentages of end members are calculated as follows. The amounts of andradite are determined from the proportion of ferric iron, pyrope from Mg, almandine from ferrous iron, and spessartine from Mn. The remainder of Al and Ca gives the amounts of grossular. The proportion of Si is always in the range of 2.90

TABLE 1. EXAMPLES OF GARNET ANALYSIS WITH THE ELECTRON MICROPROBE

No.	1	2	3	4	5	6	7	8	9	10	11	12	13
$\text{SiO}_2$	37.7%	36.8	36.9	37.6	37.0	37.1	37.0	36.7	37.1	36.5	38.6	37.8	37.3
$\text{Al}_2\text{O}_3$	20.9	20.9	20.5	20.7	20.9	19.8	19.8	19.0	20.0	19.4	19.3	19.4	19.9
$\text{FeO}^*$	3.5	7.0	7.6	6.0	7.3	6.5	7.1	7.5	12.4	13.7	7.2	9.9	16.1
$\text{MnO}^\dagger$	3.5	9.5	15.7	7.6	13.2	11.2	17.7	22.3	10.6	14.3	2.7	4.6	7.4
$\text{MgO}$	0.0	0.0	0.1	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
$\text{CaO}$	32.9	24.3	19.1	27.6	20.7	24.1	17.8	13.3	19.1	15.0	32.5	27.3	18.7
Total	98.5	98.5	99.9	99.5	99.2	98.7	99.4	98.8	99.2	98.9	100.3	99.0	99.4
Numbers of cations on the basis of 12 oxygens													
Si	2.94	2.93	2.94	2.94	2.94	2.95	2.96	2.99	2.97	2.96	2.97	2.97	2.98
Al	1.92	1.96	1.93	1.91	1.96	1.86	1.87	1.82	1.89	1.86	1.75	1.79	1.87
$\text{Fe}^{3+}$	0.08	0.04	0.07	0.09	0.04	0.14	0.13	0.18	0.11	0.14	0.25	0.21	0.13
$\text{Fe}^{2+}$	0.15	0.43	0.44	0.30	0.44	0.29	0.35	0.33	0.72	0.79	0.21	0.45	0.95
Mn	0.23	0.64	1.06	0.50	0.89	0.75	1.20	1.54	0.72	0.98	0.17	0.31	0.50
Mg	0.00	0.00	0.01	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ca	2.74	2.07	1.63	2.31	1.77	2.05	1.53	1.16	1.64	1.31	2.68	2.30	1.60
Mol. % of end members													
Pyrr.	0.0	0.0	0.3	0.0	0.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Alm.	5.0	14.3	14.5	10.0	14.8	9.6	11.7	11.0	23.8	26.3	6.9	14.8	31.5
Spess.	7.6	21.3	35.2	16.8	29.7	25.1	40.0	51.2	23.9	32.7	5.8	10.2	16.7
Gross.	83.2	62.5	46.4	68.5	53.4	58.3	41.9	28.7	46.5	33.7	74.5	64.6	45.4
And.	4.1	1.8	3.7	4.6	1.9	7.0	6.4	9.1	5.8	7.2	12.7	10.5	6.5
Compositional zoning													
	(core)												

\* Total Fe as FeO

Nos. 1-5: HS72081807 garnet-clinopyroxene skarn from the Kannon deposit, Kuga mine. Scanning profile of Al, Mn and Ca from the core (No. 1) to rim (No. 5) is shown in Figure 3. Nos. 6-8: HS72081818 garnet-clinopyroxene skarn from the Taiho deposit, Kuga mine.

Nos. 9-10: HS72081624 garnet-amphibole-fluorite skarn from the Akemidan deposit, Fujigatani mine. Nos. 11-13: HS72072307 garnet-clinopyroxene skarn from the Kagata mine.

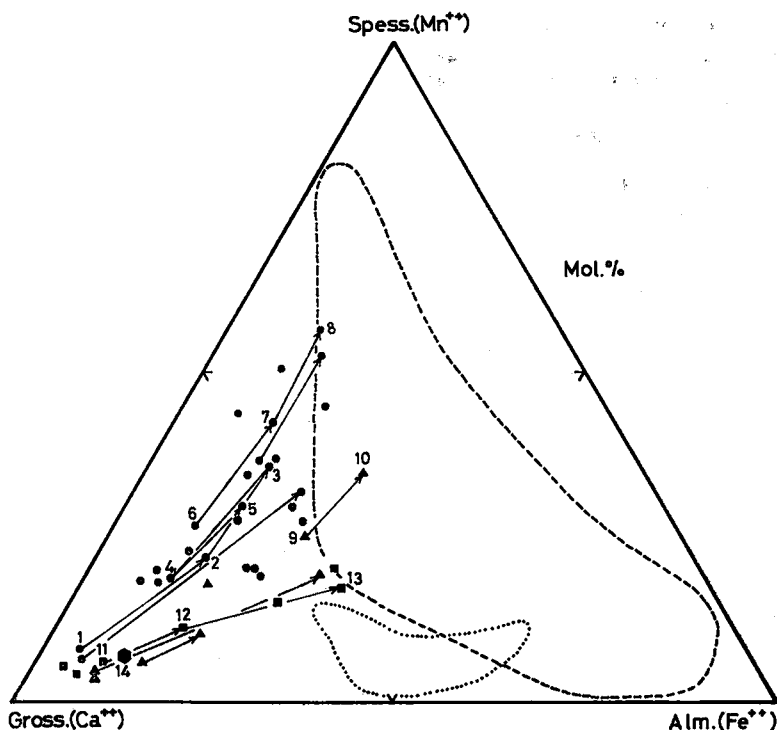


FIG. 2. Compositions of analyzed garnets. Solid circles: garnets from the Kuga mine; solid triangles: the Fujigatani mine; solid squares and hexagon: the Kagata mine; solid hexagon (No. 14) is the wet-chemical analysis (Table 2) of the Kagata mine garnet separate which contained the zoned grain plotted as Nos. 11-13. Dashed and dotted lines are the same as those in Figure 1. Arrows show the trend of the compositional zoning from core to rim. Numbers correspond with those in Table 1.

to 3.00, and is not included in the above calculations.

Andradite mol. % in the analyzed garnets from the three mines ranged from 0.0 to 16.6, and was less than 10 in most cases. Pyrope

mol. % was also very low, usually less than 0.5. The results are plotted on the almandine-spessartine-grossular triangle (Fig. 2). As shown in this Figure, the compositions of garnets from these three mines extend from the grossular

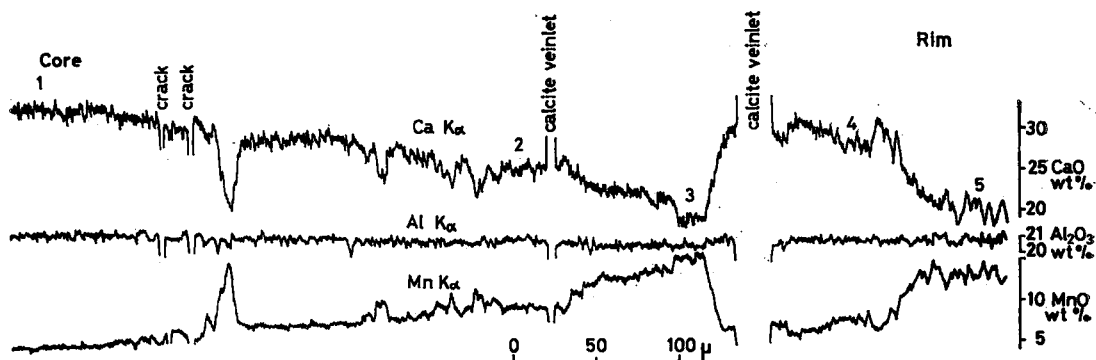


FIG. 3. Electron probe scanning profile of garnet crystal in specimen HS72081807 of garnet-clinopyroxene skarn from the Kuga mine. The result of point analysis at points Nos. 1-5 is given in Table 1 and plotted in Figure 2.

corner to the area reported by Brown (1969) as the range of the compositional variation of garnets from greenschist-facies terrains. The garnets studied commonly show compositional variation between and within grains in a single polished section: in some a remarkable compositional zoning is observed from core to rim of euhedral to subhedral crystals. Selected analyses to demonstrate such compositional zoning are given in Table 1. A crystal in a specimen (HS72081807) from the Kuga mine showed the rather complicated zoning pattern given in Figure 3. The compositions of five points in the crystal are given in Table 1 and plotted in Figure 2.

The result of conventional wet-chemical analysis of garnet separated from a specimen (HS72072307) of garnet-clinopyroxene skarn from the Kagata mine is given in Table 2, and

decrease in Mn content from core to rim (e.g. Brown 1969).

## DISCUSSION

Little has been reported previously as to temperature-pressure conditions for skarn formation in the Kuga, Fujigatani and Kagata mines. From the intimate association with granitic intrusions, the deposits are thought to have genetic relationships to them. As andalusite is found in the contact aureoles in both Kuga and Fujigatani, and Kagata areas (Takimoto 1939; Takahashi & Ueno 1960), pressure could be estimated as lower than several kbar. Ito (1962) compared the mineral assemblages of the skarns in the Fujigatani and Kuga mines with those of regionally metamorphosed calcareous rocks in Abukuma plateau described by Miyashiro (1953a), and concluded that grandite garnet, clinopyroxene, and wollastonite in the skarns were formed at lower temperatures than low-grade amphibolite facies in the Abukuma metamorphic belt.

Crystallization conditions for garnets also reported by Brown (1969) (greenschist facies) and by Ackermann *et al.* (1972) (greenschist to low-temperature amphibolite facies) seem to fall in the same range estimated above for the formation of the skarn minerals (Miyashiro 1973, p. 90). The compositional variations of garnets shown by Brown (1969), Ackermann *et al.* (1972) and in the present paper almost completely cover the area once believed to be a miscibility gap in the almandine-spessartine-grossular diagram (Fig. 2). It therefore appears that almandine, spessartine and grossular garnets can show almost complete solid solution even under conditions of relatively low temperatures and pressures, typically represented by conditions for greenschist facies. The same conclusion was suggested by Némec (1967), based on a compilation of wet-chemical analyses of garnets.

Ito & Frondel (1968) have synthesized garnets with intermediate compositions between spessartine and grossular under conditions of relatively low temperature and pressure, such as 550°C and 2 kbar. The experimental synthesis of garnets between almandine and grossular under relatively low temperatures and pressures has not yet been accomplished. Hariya & Nakano (1972) have shown that garnets on the almandine-grossular join can be synthesized at high temperature and pressure (1000°C, 13 and 20 kbar). Microprobe analyses have confirmed that almandine garnets with up to 50 mol. % grossular occur in high-pressure rocks such as

TABLE 2. RESULTS OF WET CHEMICAL ANALYSIS OF GARNET\*

SiO <sub>2</sub>	37.76 wt. %	Nos. of cations on the basis of 12 oxygens	Mol. % of end members
TiO <sub>2</sub>	0.14		Pyr. 1.9
Al <sub>2</sub> O <sub>3</sub>	19.63	Si 2.934	Alm. 9.0
Fe <sub>2</sub> O <sub>3</sub>	4.26	Ti 0.008	Spess. 6.2
FeO	4.20	Al 0.058	Gross. 70.4
MnO	2.85	Al 1.740	And. 12.5
MgO	0.51	Fe <sup>3+</sup> 0.249	
CaO	30.31	Fe <sup>2+</sup> 0.273	
Na <sub>2</sub> O	<0.02	Mn 0.188	
K <sub>2</sub> O	<0.02	Mg 0.059	
H <sub>2</sub> O(-)	0.00	Ca 2.523	
H <sub>2</sub> O(+)	0.44		
P <sub>2</sub> O <sub>5</sub>	0.05		
Total	100.19		

\* Garnet from garnet-clinopyroxene skarn (HS72072307), Kagata mine. Analyst: H. Haramura.

is represented as the solid hexagon in Figure 2. Compositional zoning observed in the same sample is shown as Nos. 11-13 in both Table 1 and Figure 2. The bulk composition of the garnet is very close to the composition of the core (No. 11 in Fig. 2) of a grain from the same specimen. This may indicate that the volumes of the rims, which are relatively rich in Mn and Fe<sup>2+</sup>, are small as compared with the volumes of the cores. However, the differences may have been exaggerated, because the rims are more magnetic than the grossular-rich cores and tend to be taken away with clinopyroxene during isodynamic separation.

The pattern of the compositional zoning in the garnets studied is usually simple, that is, Ca mol. percentages decrease, and Mn and Fe<sup>2+</sup> mol. percentages increase gradually from core to rim. In contrast, garnets from low-grade metamorphic rocks generally show a continuous

glaucophane schists and eclogites (Dudley 1969; Heritsch 1973).

As demonstrated theoretically by Miyashiro (1953b) and Zemann (1962), and experimentally by Coes (1955) and Boyd & England (1959), pyrope is stable only under high-pressure conditions. The natural occurrence of garnets with compositions between pyrope and almandine is common, especially from rocks such as peridotites and eclogites, but compositions between pyrope and spessartine are almost lacking. These considerations suggest that the distinction between "pyralpsite" and "grandite" is misleading.

According to Némec (1967), scheelite skarns are known to contain grossular garnets, some of which are rich in Mn. This characteristic feature is recognized also in the Japanese skarns. Garnets plotted in Figure 1 as Nos. 4, 5 (Lee 1962) and 8 (Ashida & Onuki 1963) are associated with scheelite. This fact may indicate that the chemical environment for the precipitation of scheelite also provides favorable conditions for the formation of  $Fe^{2+}$  and Mn-bearing grossular. Only in usual ore-skarns is  $Fe^{3+}$  significant in garnets. Usually, however, scheelite skarns are poor in ferric iron, and the garnets are close to grossular in composition, possibly because these skarns are formed under oxygen fugacities lower than the pyrite-pyrrhotite-magnetite buffer (Shimazaki 1974). Thus, relatively low oxygen fugacities may account for the substitution of  $Fe^{2+}$  and Mn in grossular garnets from scheelite deposits.

As stated by Zemann (1962), the substitution for  $Al^{3+}$  by larger ions such as  $Fe^{3+}$  in the six-coordinated position in the garnet structure makes the eight-coordinated position accessible to larger ions. Thus, with the increase in the amount of  $Fe^{3+}$ , grossular with certain amounts of  $Fe^{2+}$  and/or Mn is expected to be less stable. Although Coes (1955) synthesized garnet with the composition  $Mn_3Fe_2^{3+}Si_3O_{12}$  at high pressure, the experimental work by Geller & Miller (1959) showed that only 20 mol. %  $Fe^{3+}$  could substitute for  $Al^{3+}$  in spessartine at 1250°C and atmospheric pressure. These facts would support the suggestion stated above that the lack of  $Fe^{3+}$  is essential for the formation of  $Fe^{2+}$  and/or Mn-bearing grossular under low-temperature and low-pressure conditions.

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