Evidence for immiscibility in Ti-rich garnet in a calc-silicate hornfels from northeastern Minnesota

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ABSTRACT

Calcic garnet from a calc-silicate hornfels from the contact-metamorphic aureole of the Duluth complex, northeastern Minnesota, has TiO_2 compositions ranging from 0 to 13 wt%. The concentrations of Fe, Mg, Al, Ti, and Si are highly correlated, and 93% of the total variance can be ascribed to three principal components formed by the additive component grossular and several exchange components. The first is a combination of the exchanges $TiSi_{-1}$, $MgTiAl_{-2}$, and $MgCa_{-1}$. The second represents the substitutions of Al for Fe and of Fe for Ca. The third represents the substitution of Cr for Al. Most of the variance occurs along a linear trend from $Ca_3Al_{1.72}Fe_{0.28}Si_3O_{12}$ to $Ca_3Mg_{0.33}Al_{0.67}Fe_{0.67}Ti_{1.0}Si_{2.33}O_{12}$. Within this trend, a gap in composition occurs between 6 and 12 wt% TiO_2. Separate grains of Ti-rich and Ti-poor garnet occur in contact with sharp boundaries. No exsolution lamellae were observed, however. Immiscibility appears to be blocked by the presence of Cr.

INTRODUCTION

In garnet, Fe^{2+}, Mg, Mn, and Ca generally occur in the eightfold-coordinated B site; Al, Fe^{3+}, and Cr occur in the octahedral C site; and Si occurs in the tetrahedral T site (Novak and Gibbs, 1971; Meagher, 1980). Ti-bearing garnet, though, does not follow this simple plan. Ti does not simply substitute for Al in the C site because of the different charge and size. As a result, Ti-rich garnets are low in Si, show evidence for $^{[4]}Fe^{3+}$, $^{[4]}Fe^{2+}$, and $^{[4]}Al$, and may contain Ti^{3+} (Dowty, 1971; Huggins et al., 1977a, 1977b; Schwartz et al., 1980; Locock et al., 1995).

Evidence for the site occupancy of Ti in garnet comes from a variety of spectroscopic and analytical studies of synthetic garnet and garnet from many localities and rock types. Here I describe the compositions of Ti-rich garnet from a single rock. Although the data do not provide site occupancies directly, they do indicate an additional feature present in garnet that contains Ti, namely, immiscibility. The Ti content of the garnet ranges from <1 to 13.5 wt%, with a noticeable compositional gap between about 6 and 12%.

The samples are from the drill core USS 17700 that penetrated the late Proterozoic Duluth complex and the underlying Virginia Formation in northeastern Minnesota. The Virginia Formation is a lower Proterozoic argillite that locally contains a few carbonate nodules. The argillite is unmetamorphosed northwest of Duluth, except within the contact-metamorphic aureole of the gabbroic Duluth complex, and it is regionally metamorphosed between Duluth and Minneapolis. The Ti-rich garnet sample comes from a calc-silicate hornfels at the contact with the Duluth complex in the core.

Mineral analyses were obtained by electron micro- probe using an ARL SEMQ at the Department of Earth and Space Sciences, SUNY Stony Brook, and a Cameca SX50 at the University of Tennessee, Knoxville. Internal standards included Ti-bearing andradite. Fe^{3+} was calculated with the assumption of stoichiometry; all Ti was calculated as Ti^{4+}. Na was not detected in EDS scans and was not analyzed. The garnet was assumed to be anhydrous, although grossular-andradite garnet can contain detectable amounts of H_2O (Amthauer and Rossman, 1994). A complete set of analyses may be obtained from the author.

MINERALS

The minerals in the calc-silicate nodule include garnet, wollastonite, perovskite, and diopside. The aluminous pyroxene fassaite also occurs in some areas of the sample, and minor amounts of apatite, calcite, and zirconolite are present. Although the minerals are heterogeneously distributed within the sample, the only mineral that shows great variability in composition is garnet. Labotka and Papike (1984) estimated the pressure and temperature of metamorphism at 150 MPa and ~615 °C. An estimate of the value of X_{CO_2} is based on the coexistence of wollastonite + perovskite instead of calcite + titanite, which at the estimated temperature and pressure requires the value to be <0.01.

Garnet occurs mostly as small grains <50 μm in diameter, is typically rounded, and ranges in color from pale to dark brown. The color is related to the Ti content of the garnet: Ti-rich garnet is dark, and Ti-poor garnet is pale. Figure 1A shows a back-scattered electron image of a cluster of garnet grains, which includes both a bright Ti-rich garnet and a dull Ti-poor garnet. The contact between them is sharp and cuspate.
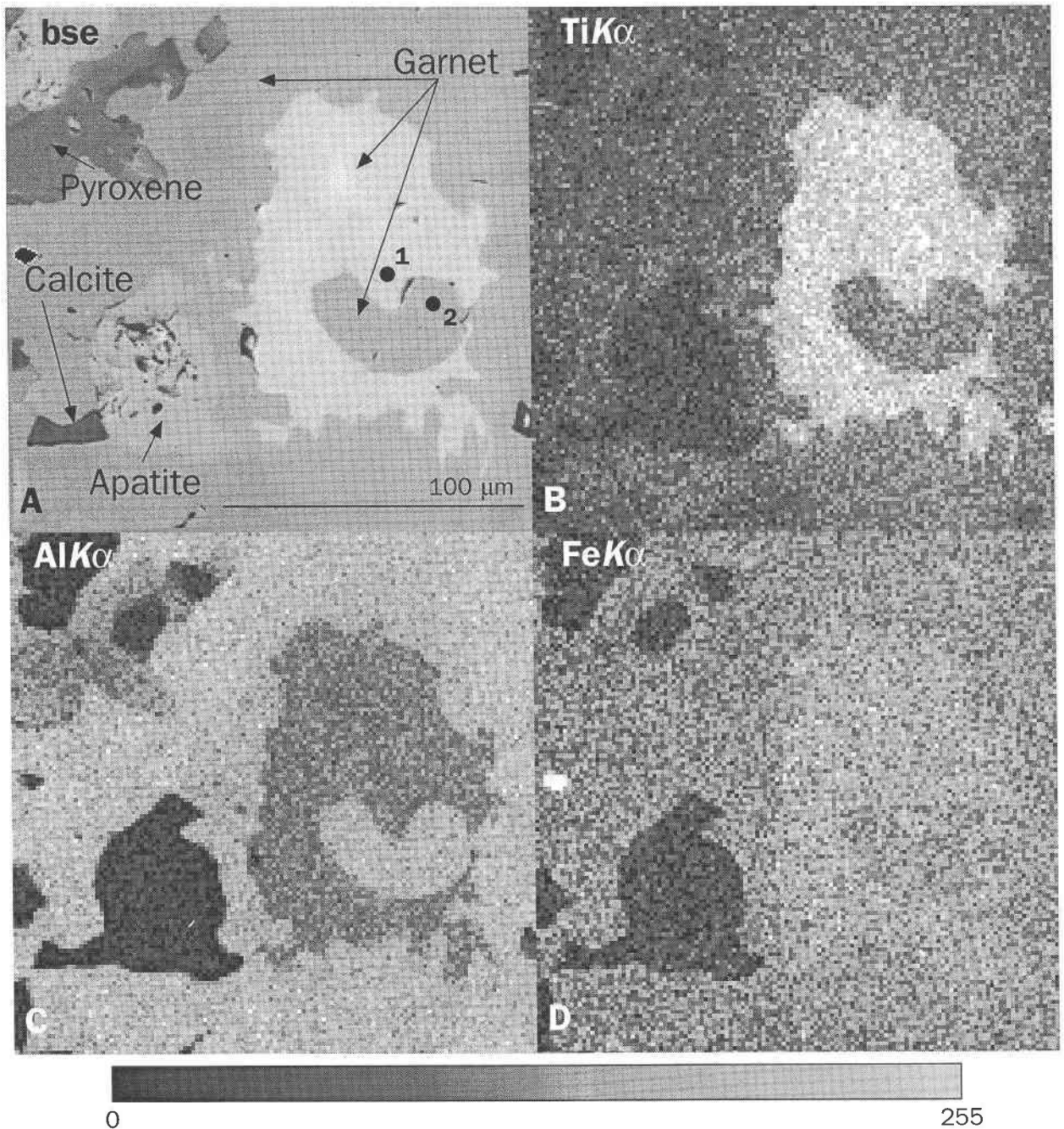
Fig. 1.   Composite garnet grains from sample V223-2, showing distinct regions of Ti-rich and Ti-poor garnet. (A) Back-scattered electron image, showing the bright Ti-rich garnet in contact with Ti-poor garnet. Other minerals are identified on the image. The locations of the analyses are indicated. (B) Ti$K\alpha$ X-ray scan. (C) Al$K\alpha$ X-ray scan. (D) Fe$K\alpha$ X-ray scan. The gray-scale bar at the bottom defines the relative X-ray intensity in images in **B**, **C**, and **D** on an 8-bit scale from 0 to 255. The gray scale of each image was stretched to correspond to the range between the minimum and maximum counts.

The compositions of garnet at the two points indicated on Figure 1A are shown in Table 1. Both garnets are Ca rich, with nearly sufficient Ca to fill the B site. The pale garnet, point 2, contains 1.9 wt% TiO_2, and the dark garnet, point 1, contains 13.4 wt% TiO_2. Si, Al, and Fe are the other major constituents. Mn is present in minor

amounts, and the calculated ratio FeO/Fe_2O_3 ranges from 0.0 to 1.0. Mg is more abundant in the Ti-rich garnet than in the Ti-poor garnet, and the high abundance of Ca seems to require that Mg occurs in the octahedral site (see Table 1). Zr and V are also present in the Ti-rich garnet, and the variation in the brightness of the Ti-rich

TABLE 1. Selected analyses of garnet in sample V223b

	Point 1* dark garnet	Point 2 pale garnet
	wt%	
SiO_2	27.89	37.45
TiO_2	13.43	1.87
ZrO_2	3.55	0.20
Al_2O_3	7.06	17.93
V_2O_3	0.75	0.09
Cr_2O_3	0.17	0.02
Fe_2O_3**	7.90	5.81
FeO	2.81	1.20
MnO	0.62	1.12
MgO	1.57	0.64
CaO	33.14	33.75
Total	98.90	100.07
	Cations pfu	
Si	2.34	2.89
Ti	0.85	0.11
Zr	0.15	0.01
Al	0.70	1.63
V	0.04	0.00
Cr	0.01	0.00
Fe^{+3}	0.50	0.34
Fe	0.20	0.08
Mn	0.04	0.07
Mg	0.20	0.07
Ca	2.98	2.79
Total	8.00	8.00

* Points are identified in Fig. 1.
** Fe_2O_3 calculated with the assumption of stoichiometry.

garnet in Figure 1A is largely the result of the variation in the ZrO_2 content.

Images of Ti$K\alpha$, Al$K\alpha$, and Fe$K\alpha$ scans are also shown in Figure 1. The Ti-rich garnet contains less Al but more Fe than the Ti-poor garnet. The relation can be seen in Table 1, but the generality of the relation can be demonstrated from the correlations among the cations.

CORRELATIONS

The compositions of garnet from three samples of the nodule were converted to a basis defined by the additive component grossular, $Ca_3Al_2Si_3O_{12}$, and the exchange components $TiSi_{-1}$, $MgTiAl_{-2}$, $FeAl_{-1}$, $CrAl_{-1}$, $FeCa_{-1}$, $MnCa_{-1}$, and $MgCa_{-1}$. The additive component was chosen because all these garnets are Ca-rich. The exchange components were chosen to constitute the sufficient total of eight components for the nine oxides (see Labotka, 1983, for a description of the method). Zr and V were not included in the new basis because they are minor components and were not analyzed in all grains. There is no crystal-chemical significance attached to the choice of exchange components, and although the abundances of Ti and Si are commonly inversely correlated, the choice of the component $TiSi_{-1}$ is not meant to imply that Ti substitutes for Si in the T site.

The chosen components may constitute a sufficient set, but they may not all be necessary. The crystal structure of garnet imposes covariance among the components to maintain a stable structure. Table 2 shows the correlation coefficients among the exchange components. The choice of exchange components rather than cation components helps to eliminate any correlations induced by closure.

Many of the coefficients in Table 2 have absolute values near one, indicating a high degree of correlation or anticorrelation among the components. The most significant correlations occur among the components $TiSi_{-1}$, $MgTiAl_{-2}$, and $MgCa_{-1}$, indicating that, in the Ti-rich garnet, Mg and Ca are increased and Al and Si are decreased relative to their values in Ti-poor garnet. The nearly linear relation among these components indicates that all the components are not necessary. There is a linear combination that reduces the number of components and accurately represents the compositional variability in the studied garnet.

Table 3 shows three eigenvectors, or principal components, extracted from the correlation matrix. The vectors are an orthogonal transformation of the basis to one in which the components are uncorrelated. The components of an eigenvector, when the sum of their squares is normalized to one, are the direction cosines of the vector.

The three vectors in Table 3 account for 93% of the total variance in the data set. The first principal component, Factor 1, represents the noted correlation among $TiSi_{-1}$, $MgTiAl_{-2}$, and $MgCa_{-1}$. Factor 2 represents the substitution of Al for Fe and of Fe for Ca, and Factor 3 represents the substitution of Cr for Al. With these vectors as guides, a component with the composition $Ca_3Mg_{0.5}$-$AlTi_{1.5}Si_2O_{12}$, which is called here Ti-Gar, was chosen to represent the variability in Ti content. This component represents grossular + $1.0TiSi_{-1}$ + $0.5MgTiAl_{-2}$. More than 90% of the variance occurs within the system grossular-andradite–Ti-Gar. Cr occurs in abundance in only a few grains, and Fe^{2+} and Mn occur as small amounts of almandine and spessartine components. The resulting mineral compositions are shown in Figure 2.

IMMISCIBILITY

The garnet compositions illustrated in Figure 2 show a nearly linear relation between $Ca_3Al_{1.72}Fe_{0.28}Si_3O_{12}$ and a

TABLE 2. Correlation matrix for garnet components

	$TiSi_{-1}$	$MgTiAl_{-2}$	$FeAl_{-1}$	$CrAl_{-1}$	$FeCa_{-1}$	$MnCa_{-1}$	$MgCa_{-1}$
$TiSi_{-1}$	1.000						
$MgTiAl_{-2}$	0.912	1.000					
$FeAl_{-1}$	0.140	0.105	1.000				
$CrAl_{-1}$	0.045	0.001	−0.214	1.000			
$FeCa_{-1}$	0.109	0.231	−0.697	0.330	1.000		
$MnCa_{-1}$	−0.190	−0.116	−0.841	−0.054	0.671	1.000	
$MgCa_{-1}$	−0.854	−0.969	−0.223	−0.035	−0.175	0.223	1.000

TABLE 3. Eigenvectors of the correlation matrix

	Factor 1	Factor 2	Factor 3
$TiSi_{-1}$	0.906	0.261	-0.042
$MgTiAl_{-2}$	0.923	0.350	-0.108
$FeAl_{-1}$	0.444	-0.830	0.059
$CrAl_{-1}$	-0.010	0.310	0.943
$FeCa_{-1}$	-0.074	0.916	0.089
$MnCa_{-1}$	-0.462	0.776	-0.346
$MgCa_{-1}$	-0.941	-0.253	0.035
Total variance (%)	42.5	35.4	14.8

garnet with the composition $Ca_3Mg_{0.33}Al_{0.67}Ti_{1.0}Fe_{0.67}$-$Si_{2.33}O_{12}$, that is, ⅓ andradite + ⅔ Ti-Gar. The exceptions are grains that either contain substantial quantities of Cr, as indicated on the figure, or fall on the grossular-andradite join. Ti-bearing garnet shows a distinct gap in Ti content from ~6 to ~12 wt% TiO_2, which corresponds to ~0.4 to 0.7 cations pfu. The difference in TiO_2 content is even greater in the garnet grains shown in Figure 1. The wide range in garnet composition within the sample indicates that only local equilibrium could have been attained. However, the grains in Figure 1 are in contact along a sharp boundary, which suggests that the grains were in equilibrium with each other along that contact. There are numerous examples of similar boundaries between grains with compositions on either side of the gap in TiO_2 content in these samples. There are also many examples of grains that are abruptly zoned in composition from Ti-rich cores to Ti-poor rims. The solid solution between Ti-rich garnet and Ti-free garnet appears to possess a region of immiscibility.

The most Ti-rich compositions observed have just fewer than 1.0 Ti pfu, but it is not clear whether this represents the maximum possible Ti content. The abundance of the component $TiSi_{-1}$ is buffered by the coexistence of wollastonite and perovskite, and the abundance of the component $MgTiAl_{-2}$ is determined by the equilibrium $MgTiAl_{-2}$ + grossular = wollastonite + perovskite + diopside, although the variance of this equilibrium is higher than that for the $TiSi_{-1}$ equilibrium. The andradite component does not appear to be buffered by the mineral assemblage. The peculiar combination of these components that produces the linear trend seen in Figure 2 must be a consequence of the constraints of the crystal structure on composition.

Likewise, the occurrence of a gap in the solid solution must be a consequence of the structural constraints. The limits of the gap are at ~⅓ and ¾ along the trend, as indicated in Figure 2. The region of metastable and unstable compositions must be related to differences in the polyhedral sizes induced by the substitutions. The sites occupied by the cations cannot be determined from the analytical data alone; Al, Ti, Fe^{2+}, or Fe^{3+} must substitute for Si, but this study cannot determine how much of each occupies the T site. Locock et al. (1995) indicated that only Fe^{2+} and Fe^{3+} substitute for Si, but the garnet studied by them contains little Al. If the preference for
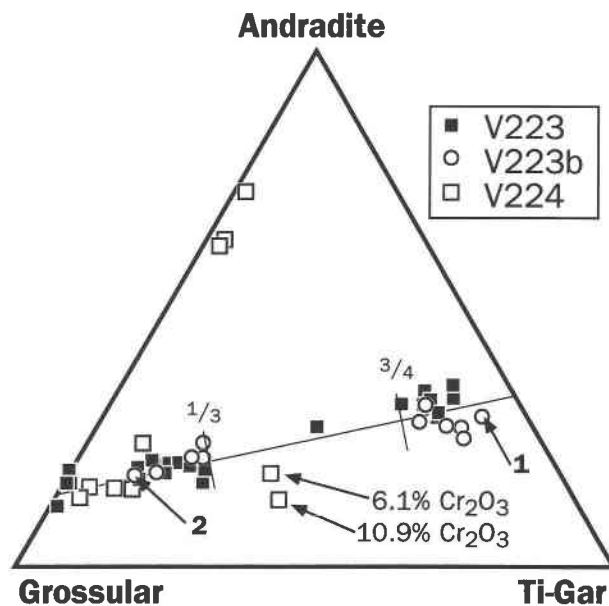

Fig. 2. Garnet compositions plotted on the triangle grossular $(Ca_3Al_2Si_3O_{12})$–andradite $(Ca_3Fe_2Si_3O_{12})$–Ti-Gar$(Ca_3Mg_{0.5}AlTi_{1.5}$-$Si_2O_{12})$. This system represents 90% of the variance in observed compositions. Points 1 and 2 are the analyses shown in Fig. 1A and in Table 1. Cr_2O_3 contents are indicated for the analyses that fall within the gap.

tetrahedral site occupancy is as suggested by Huggins et al. (1977b) and only [4]Al substitutes for [4]Si, then the relative difference in the mean radius of the octahedral cation between the end-member compositions along the join shown in Figure 2 is +16%, and the difference for the tetrahedral cation is +24%. The presence of [4]Fe^{2+} or [4]Ti does not alleviate the large difference between $\Delta<[6]r>$ and $\Delta<[4]r>$. The existence of limited solid solution in this system, then, is not surprising.

Immiscibility would also be indicated by the presence of exsolution lamellae, but no lamellae were observed at the micrometer scale. Either the reaction rate for exsolution was too slow or the limbs of the solvus are steep over the temperature interval of metamorphism. The solvus also appears to be limited by the presence of Cr^{3+}. Grains that contain both Ti and Cr have compositions that lie within the miscibility gap (Fig. 2). Analyses discussed by Dowty (1971) and Schwartz et al. (1980) do not show evidence for the gap, but Cr contents were not reported by them. Synthetic garnet studied by Huggins et al. (1977a) showed no evidence for immiscibility on the joins grossular-$Ca_3Fe_2Ti_{1.42}Si_{1.58}O_{12}$ and andradite-$Ca_3Fe_2Ti_{1.42}Si_{1.58}O_{12}$ at 1050 °C. One sample described by Huggins et al. (1977b) from San Benito County, California, contains garnet with a dark core and a pale rim with a sharp contact between them. All other garnet grains have compositions on one side or the other of the gap shown by the Minnesota samples. None of those from Huggins et al. (1977b) contains appreciable Cr. Van Baalen (1991) reported the compositions of garnet from sev-

eral serpentinite localities and outlined a compositional region devoid of samples. He indicated the possible existence of immiscibility at low temperature. Although it is difficult to compare the region outlined by van Baalen with that reported here, he recognized that the proposed immiscible region occurs within the three-component region grossular-andradite-schorlomite. The immiscibility within titanian garnet seems to require the presence of Al and the absence of Cr. Ti-bearing garnet commonly occurs in many alkalic igneous rocks and is called either melanite if $Fe^{3+} > Ti$ or schorlomite if $Fe^{3+} < Ti$ (Deer et al., 1992). The distinction between melanite (e.g., point 2 in Fig. 1) and schorlomite (point 1 in Fig. 1) may be a natural consequence of immiscibility in Ti-bearing garnet.

ACKNOWLEDGMENTS

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