

Mineral chemistry of igneous melanite garnets from analcite-bearing volcanic rocks, Alberta, Canada

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Abstract. The mineral chemistry of melanite garnets from the Crowsnest volcanic rocks of SW Alberta, Canada, has been investigated by using electron microprobe scans, quantitative analyses and multivariate statistical analysis. The garnets occur with aegirine-augite, sanidine, analcite and rare plagioclase as phenocrysts in trachyte and phonolite flows, agglomerates and tuffs. Wavelength dispersive microprobe scans reveal complex zonation patterns, both normal and oscillatory. The results of fifty quantitative analyses were subjected to R-mode factor analysis to delineate the chemical exchanges producing the zonation. The chemical zonation of the garnets may be attributed to four independent binary exchanges; Al–Fe³⁺, Si–Ti, Ca–Mn and Mg–Fe²⁺. The stoichiometry of these garnets, based on microprobe and wet chemical Fe analyses, combined with the strongly antithetic behavior of Si and Ti lead us to infer that the Ti in these garnets is dominantly tetravalent. It is clear from this study that quantitative modelling of the processes of crystal growth and zonation of melanite garnets in alkaline, undersaturated igneous rocks should be aimed at simulating the four chemical exchanges listed above.

Introduction

Titanium-bearing andradite garnets occur in a wide variety of parageneses. The majority of titanium-rich andradite garnets are found principally in extrusive and intrusive alkaline igneous rocks and related types (e.g. Huggins et al. 1977a, b; Deer et al. 1982; Meagher 1982). Andradite garnets low in TiO₂ occur in skarns (Deer et al. 1982) and more rarely in serpentinitized peridotite bodies (Howie and Woolley 1968; Manning and Harris 1970). In these latter cases, the garnets are believed to be of metamorphic or metasomatic origin (Deer et al. 1982); however, the Ti-rich garnets in undersaturated alkaline igneous rocks are undoubtedly primary (Deer et al. 1982). The rarity of Ti-bearing garnets, their unusual occurrences and the fact that they contain Ti, a cation not normally present in garnets, have prompted studies of their mineral chemistry (e.g. Howie and Woolley 1968; Gomes 1969), zoning patterns (e.g. Gomes 1969), mineral stability (Virgo and Huckenholz 1974) and the site occupancy of Ti, Al and Fe³⁺ (Huggins et al. 1977a, b).

The mineral chemistry of melanite-schorlomite garnets has been investigated by a number of workers (Lehijärvi 1966; Howie and Woolley 1968; Isaacs 1968; Gomes 1969; Huggins et al. 1977a, b; Schwartz et al. 1980). In general, no consensus of opinion has been reached on the nature and origin of mineral chemical zonation in these garnets. It is possible that a large part of the disagreement in the literature is due to the diversity of parageneses of melanite-schorlomite garnets (see summary in Deer et al. 1982, p. 639–641). Current discussion of the mineral chemistry of melanite garnets from alkaline volcanic rocks concerns two questions. Firstly, what is the distribution of Al, Fe and Ti amongst the octahedral, tetrahedral and 12-fold coordination sites in these garnets and what principal exchanges are responsible for variations in the proportions of these and other elements in these garnets? Secondly, what combination of intensive parameters (e.g., oxygen fugacity, P(H₂O), temperature and pressure) are required to stabilize these garnets in alkaline igneous melts?

This paper describes the mineral chemistry and chemical zoning of melanite garnet phenocrysts in the Crowsnest volcanic rocks, Alberta, Canada. We also present results of multivariate statistical analysis of the data set, which provide an insight into the chemical exchanges which produce the zoning. Finally, we make inferences regarding the site occupancy and valence state of titanium in these garnets, based on quantitative analyses. In the absence of igneous phase relations of grossular-titanium andradite solid solution and cation diffusion coefficients in alkaline melts, we do not attempt to model the zoning.

Geological setting and petrography

The geological setting and petrographic features of the Crowsnest volcanic rocks have been described by Pearce (1967, 1970) and Ferguson and Edgar (1978). The volcanic rocks occur in the foothills of the Rocky Mountains, Alberta (Fig. 1) as a sequence of agglomerates with subordinate lava flows, tuffs and volcanoclastic sediments. The Crowsnest Formation overlies and interfingers with the sandstones of the Lower Cretaceous Blairmore Group and is overlain by the black shales of the Upper Cretaceous Alberta Group (Pearce 1967, 1970). Sanidine phenocrysts from the Crowsnest volcanic rocks have been dated at 96 Ma by the K–Ar method (Folinsbee et al. 1957). The volcanic rocks are alkaline and are predominantly trachytes in the lower part of the formation with phonolites and anal-

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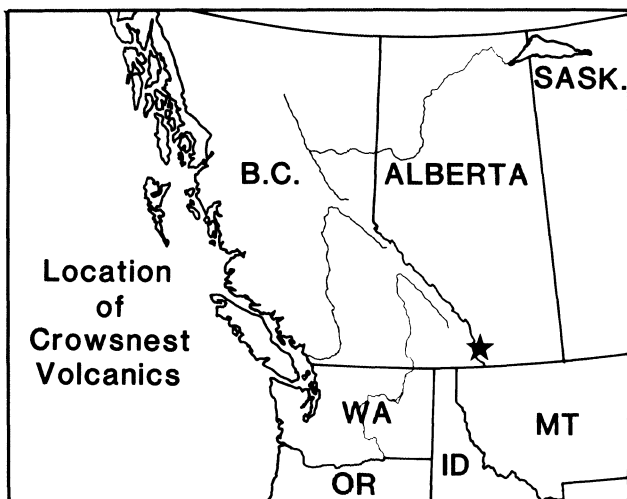


Fig. 1. Location of the Cretaceous Crowsnest Formation

cite phonolites (blairmorites) becoming more abundant in the upper part of the formation.

The volcanic rocks contain abundant phenocrysts of sanidine, aegirine-augite, analcite (in blairmorites), melanite garnet and rare plagioclase within an altered groundmass. Phenocryst assemblages are variable in different rock types. Phenocrysts of sanidine and garnet in tuffs are often large reaching 50 mm and 7.5 mm, respectively. Analcite phenocrysts attain a size of 30 mm in some blairmorites.

In thin section, the sanidine phenocrysts are euhedral to subhedral, optically zoned and slightly altered. Pyroxene phenocrysts (aegirine-augite) are subhedral, in some cases slightly altered to carbonate, compositionally zoned, and often have cores of augite (Pearce 1970). Pyroxenes contain abundant inclusions of garnet, magnetite, sphene, apatite and analcite. Zoned analcite phenocrysts only occur in blairmorites and some phonolites where they are euhedral to subhedral trapezohedrons.

Garnet phenocrysts are extremely fresh, perfectly euhedral (dodecahedral) in most cases, twinned and intricately zoned on a scale of 30–50 μm . They range in size from microphenocrysts (0.1 mm) to phenocrysts 7.5 mm in diameter. Garnets are red/brown in color and essentially isotropic. However, color varies from zone to zone within each garnet indicating that the coloration depends on the chemical zonation. Garnet phenocrysts contain a wide variety of included minerals (aegirine-augite, sanidine, mica, Fe–Ti oxides, analcite, sphene, apatite and sulfide minerals).

The groundmass of all rock types, unlike the phenocryst phases, is fine grained and often highly altered to clay minerals, with small crystals of aegirine-augite and sanidine. In some trachytic members, the groundmass minerals are crudely aligned. Other accessory minerals in the groundmass are magnetite, apatite, sphene, carbonate and sulfides.

Note on nomenclature

Ti-rich garnets belonging to the grossular-andradite series have been variably referred to as melanites, ivaarites, schorlomites and Ti-rich andradites. Distinction between these names on the basis of site occupancy is confused due to disagreements in the literature regarding the location and valence of Fe and Ti in these garnets. In this paper, we adopt the suggestion of Howie and Woolley (1968) that garnets with up to 1.0 formula units of Ti per 24 oxygens be termed melanites.

Analytical methods

The mineral chemistry of the Crowsnest garnets was investigated by electron microprobe analysis. Fifty quantitative energy dispersive analyses (EDA) were obtained on 20 garnets using an ARL-SEMQ microprobe equipped with an EEDS-ORTEC energy dispersive system and operating conditions of 15 kV accelerating voltage, 4 nA sample current, 240 second count times, and a 1–2 μm beam diameter. The mineral standards were pyrope (Mg), grossular (Ca, Al, Si), ilmenite (Fe, Ti) and willemite (Mn); and full ZAF corrections were applied to the energy dispersive spectra using EDATA2 (Smith and Gold 1979). The detection limit using the above operating conditions for EDA is approximately 500 ppm, and accuracies for major and minor elements are comparable to wavelength dispersive analysis (Smith 1976). Wavelength dispersive X-ray line scans were conducted across zoned garnets using an ARL-EMX microprobe with operating conditions of 15 kV accelerating voltage, 24 nA sample current and a scan speed of 8 $\mu\text{m}/\text{min}$. Wavelength dispersive scans were made for Na and Cr but neither was detected.

Wet chemical analysis for ferrous iron was performed on whole garnet samples using the meta-vanadate titration method of Wilson (1960).

Results

Mineral chemistry

Representative garnet compositions are presented in Table 1. The ranges of oxide concentration for each element (in wt %) are as follows: MgO (0.12–0.75), Al_2O_3 (1.31–9.27), SiO_2 (32.7–35.9), CaO (32.0–34.1), TiO_2 (2.46–7.73), FeO (1.40–2.19), Fe_2O_3 (15.8–24.6) and MnO (0.27–0.96).

Zoning profiles

Garnets are intricately chemically zoned, having a small core discontinuously overgrown by a broad rim (Figs. 2 and 3). Within the core, Mn and Al are enriched and Ti and Fe are depleted. At the boundary of the core, Mn and Al decrease and Ti and Fe increase sharply. Within the broad rim, all elements have oscillatory zoning superimposed upon a “normal”-type zoning pattern whereby Mn and Al increase and Ti and Fe decrease toward the edge of the garnet. Zonations in Ca and Si are not large; however, Si increases (15.7–16.3 element %) and Ca decreases (24.3–23.0 element %) towards the rim.

In previous studies, color differences in the zones of melanite garnets have been attributed to the concentration of Ti (e.g. Gomes 1969; Pearce 1967, 1970): dark zones have high concentrations of Ti and light colored zones are poorer in Ti. We also confirmed this effect (Figs. 2 and 3). Gomes (1969) conducted a study of zoning in melanite garnets from nepheline syenites and reported similar oscillatory and normal zoning of elements.

Substitutions

Strong negative correlations exist between the element pairs Ca–Mn, Al–Fe and Si–Ti (Fig. 4, Table 2), having correlation coefficients of -0.804 , -0.884 and -0.857 , respectively. However, there are also several minor correlations. The major negative correlations undoubtedly represent exchanges but the minor correlations may or may not represent coupling in substitutions.

Since a correlation coefficient matrix cannot distinguish between these potential couplings or possible induced corre-

Table 1. Representative microprobe analyses of garnets^a

Oxide	1	2	3	4	5	6	7	8
SiO ₂	32.7	33.0	35.9	35.3	33.9	33.4	34.8	33.5
TiO ₂	6.77	7.73	3.06	2.46	4.06	5.63	3.46	4.00
Al ₂ O ₃	1.31	4.44	9.27	3.57	2.55	2.40	2.31	2.10
Fe ₂ O ₃	23.3	18.7	15.8	22.7	24.2	22.4	23.4	24.6
FeO ^b	2.08	1.66	1.40	2.02	2.15	1.99	2.08	2.19
MnO	0.41	0.40	0.61	0.32	0.96	0.47	0.27	0.84
MgO	0.25	0.75	0.50	0.27	0.31	0.12	0.24	0.14
CaO	32.5	32.7	33.5	34.1	32.4	33.1	33.4	32.0
Total	99.32	99.38	100.04	100.74	100.53	99.51	99.96	99.37

Structural formula based on 8 cations								
O	12.02	12.04	12.00	11.98	11.99	12.00	11.97	12.05
Si	2.78	2.75	2.89	2.92	2.83	2.81	2.90	2.83
Ti	0.43	0.48	0.19	0.15	0.26	0.36	0.22	0.25
Al	0.13	0.44	0.88	0.35	0.24	0.24	0.23	0.21
Fe ³⁺	1.49	1.17	0.96	1.41	1.53	1.42	1.46	1.56
Fe ²⁺	0.15	0.12	0.09	0.14	0.15	0.14	0.15	0.16
Mn	0.03	0.03	0.04	0.02	0.06	0.03	0.02	0.06
Mg	0.03	0.09	0.06	0.03	0.03	0.02	0.03	0.02
Ca	2.96	2.92	2.89	2.98	2.90	2.98	2.99	2.90

^a Two standard deviation errors are: Mg (10.3%), Al (2.80%), Si (0.76%), Ca (0.79%), Ti (2.30%), Mn (12.6%), Fe (1.30%)

^b FeO determined by the wet chemical method of Wilson (1960)

0.5mm

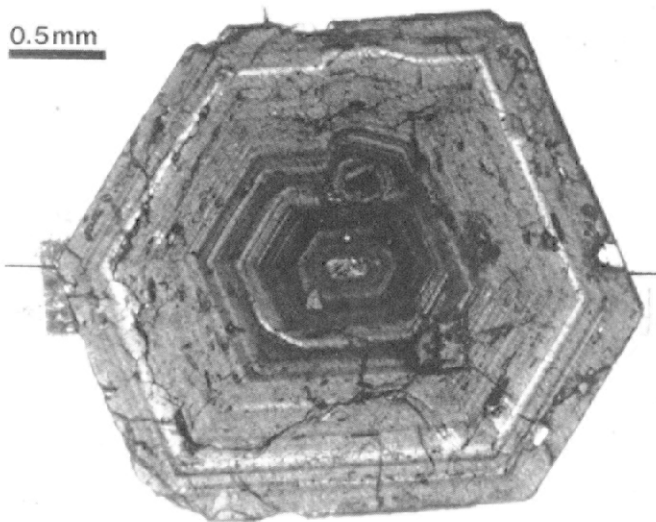


Fig. 2. Photomicrograph of a polished grain mount of a typical zoned melanite garnet from the Crownsnest volcanic rocks. The two black lines represent the line of a microprobe traverse

lations (closure) between these elements, we performed R-mode factor analysis on the garnet analyses. Coupled substitutions should show up as large factor loadings in the results of the analysis (Table 3). Factor 1 has high (>0.5) loadings for Al (0.876) and total Fe (-0.954) and accounts for 29.4% of the total variance. There are minor (0.2–0.5) loadings for Mg (0.374), Si (0.265), and Mn (0.383). Clearly, the principal exchange represented by this factor, is Al for Fe. Factor 2 has high loadings for Si (0.940) and Ti (-0.964), and a minor loading for Al (0.360). This factor accounts for 28.8% of the variance. The principal exchange is clearly Si for Ti. Factor 3 has high loadings for Ca (0.983)

and Mn (-0.888), a minor loading for Al (-0.248), and accounts for 26.5% of the variance. As with factors 1 and 2, factor 3 appears to represent a simple, binary exchange, in this case, Ca for Mn. Factor 4 has a high loading for Mg (-0.916) and a minor loading for Fe (0.292). We interpret this factor as an exchange of Mg for Fe²⁺. The use of total Fe in the factor analysis discriminates against a high rating for the Mg-Fe²⁺ exchange factor because the variance of Fe due to this exchange is masked by the much larger contribution to the variance from the Al-Fe exchange. This is simply due to the higher concentration of Fe³⁺. If we could include individual terms for ferric and ferrous iron in the factor analysis, from individual determinations of FeO for each analysis spot, then the Mg-Fe²⁺ exchange might be more distinct. Factors 5 and 6 are insignificant as their eigenvalues are 0.09 and 0.05, respectively, and there are no large or minor factor loadings for either. Together, factors 1 to 4 account for 99.1% of the variance in the data set leaving less than 1% to be taken up by factors 5 and 6. We infer from these results that the variable chemistry of these garnets is dominated by four binary exchanges; Al-Fe³⁺, Si-Ti, Ca-Mn and Mg-Fe²⁺.

Stoichiometry

Calculation of the stoichiometry and site assignment of cations in melanite garnets is a problem due to the uncertainty of the valence states and location of Fe and Ti in the garnet structure (e.g. Huggins et al. 1977a, b). There is little agreement in the literature regarding a standard technique for assigning Ti, Al and Fe to relevant sites (e.g. Huggins et al. 1977a, b; Deer et al. 1982). On the basis of Mössbauer spectra Huggins et al. (1977a) regarded the tetrahedral site preference in melanite garnets to be Al ≥ Fe³⁺ > Ti and proposed that Fe²⁺ was also present in the tetrahedral site. However, Huggins et al. (1977b) stated that the Si⁴⁺-Ti⁴⁺

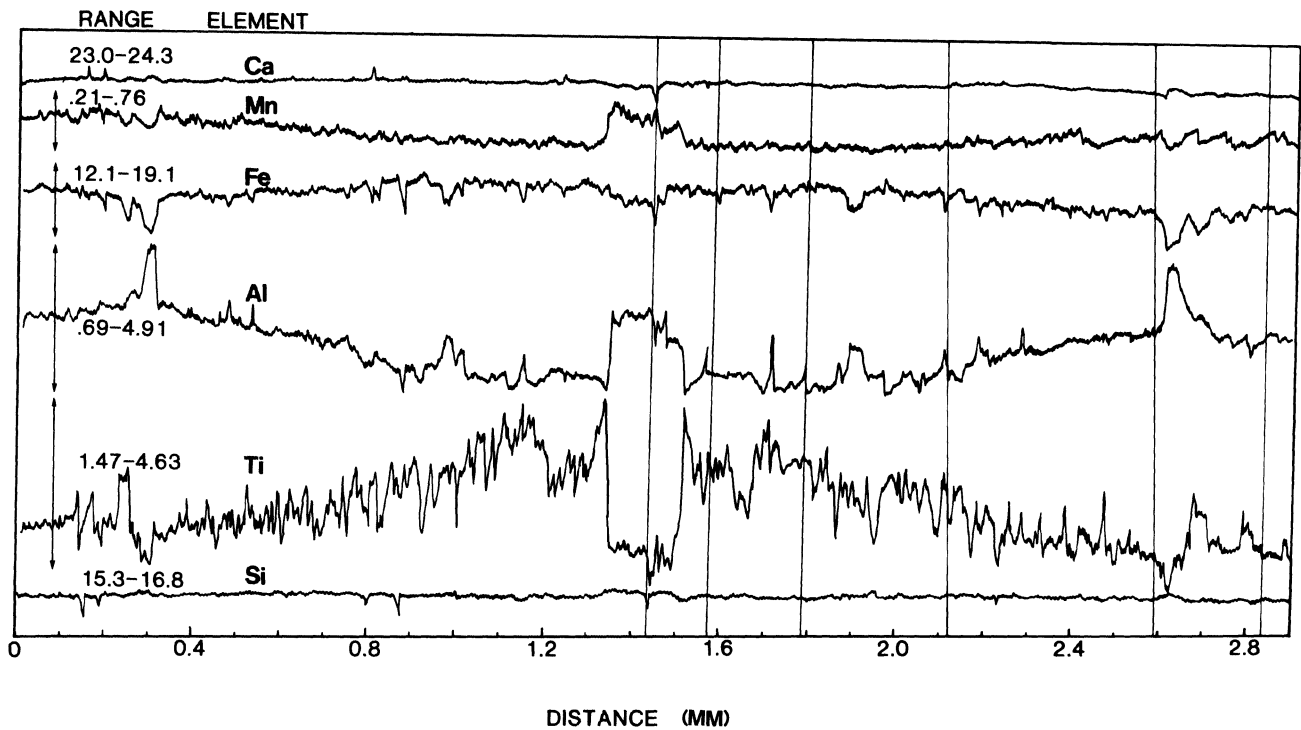


Fig. 3. Wavelength dispersive microprobe scans across a garnet for Ca, Mn, Fe, Al, Ti and Si (operating conditions are quoted in the text). The vertical lines show the locations of quantitative analyses. The arrows on the Mn, Fe, Al and Ti profiles show the range in wt% of the element for the profile

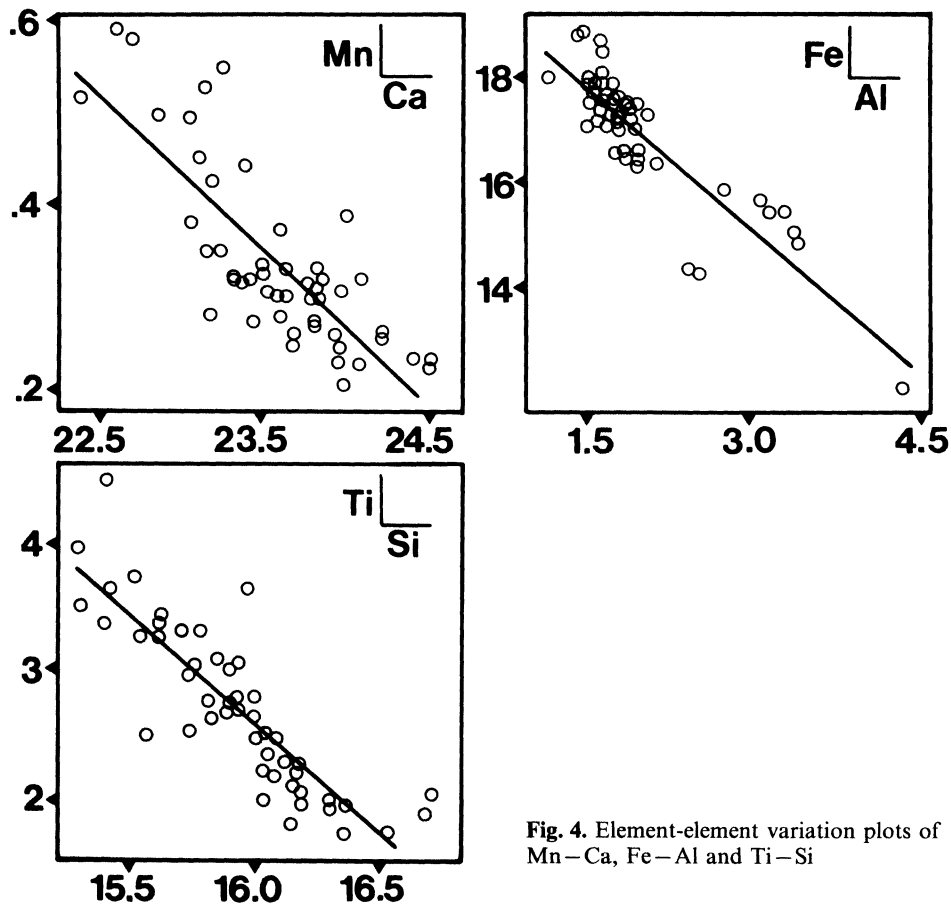


Fig. 4. Element-element variation plots of Mn-Ca, Fe-Al and Ti-Si

Table 2. Correlation coefficient matrix

	Mg	Al	Si	Ca	Ti	Mn	Fe
Mg	1.000						
Al	0.462	1.000					
Si	-0.051	0.538	1.000				
Ca	-0.070	-0.156	0.211	1.000			
Ti	0.299	-0.321	-0.857	0.012	1.000		
Mn	0.083	0.606	0.169	-0.804	-0.264	1.000	
Fe	-0.628	-0.884	-0.230	-0.042	-0.111	-0.355	1.000

Table 3. R-mode factor matrix for fifty analyses and seven elements

Element	F1	F2	F3	F4	F5	F6
Mg	0.374	-0.145	-0.022	-0.916	0.005	0.004
Al	0.876	0.360	-0.248	0.198	-0.031	0.007
Si	0.265	0.940	0.100	0.014	0.187	0.003
Ca	0.076	0.094	0.983	0.069	0.009	0.116
Ti	0.032	-0.964	0.114	-0.162	0.172	0.017
Mn	0.383	0.166	-0.888	0.059	0.011	0.180
Fe	-0.954	0.028	0.010	0.292	0.045	-0.018
Eigenvalue	2.06	2.02	1.85	1.01	0.09	0.05
% Variance	29.4	28.8	26.5	14.4	<1.0	<1.0
Cum. Var.	29.4	58.2	84.7	99.1	99.9	100.0

exchange is the predominant manner in which Ti is introduced into the garnet structure. From the data presented here, this exchange appears to be dominant.

Therefore, in this study, we chose to calculate garnet molecules according to the following scheme, based on the diadochies inferred from factor analysis: The raw element analyses (using Fe^{2+}/Fe^{3+} determined from wet chemistry) were cast to 8 cations. Oxygen obtained by stoichiometry was 12 ± 0.05 formula units for all analyses. All Si was assigned to the tetrahedral site (Z) along with sufficient Ti to fill the site with 3.0 cations. Since all analyses had $Si + Ti > 3.0$, remaining Ti was allocated to the Y site. All Ca was assigned to the X site. Where Ca was insufficient to fill this site, Mn, and, if necessary, Mg was assigned to this site. All ferric and ferrous iron, and Al were assigned to the Y site.

The resulting garnets are essentially grossular (Gr)–Ti-rich andradite (Ti–Ad) binary solid solutions (Gr+Ti–Ad=96.0–99.3 mole percent) which range from Ti–Ad₉₃Gr₆ to Ti–Ad₅₇Gr₄₀. The minor components are represented by spessartine and pyrope (Sp+Py) with Sp+Py ranging from 0.7 to 4.0 mole percent.

Discussion

The range of compositions of Crowsnest garnets is presented in Fig. 5 as mole proportions of Ti-andradite, grossular and spessartine+pyrope. The garnets range from 55 to 95 mole percent Ti–Ad with up to 4.0 mole percent Sp+Py. The majority of analyses cluster about a composition of Ti–Ad₈₅–Gr₁₃–Sp+Py₂. The Crowsnest garnets span the entire compositional range of melanites from other localities (Figs. 5 and 6). However, the TiO₂ content of Crowsnest garnets is relatively restricted with respect to the range of TiO₂ contents of the other localities.

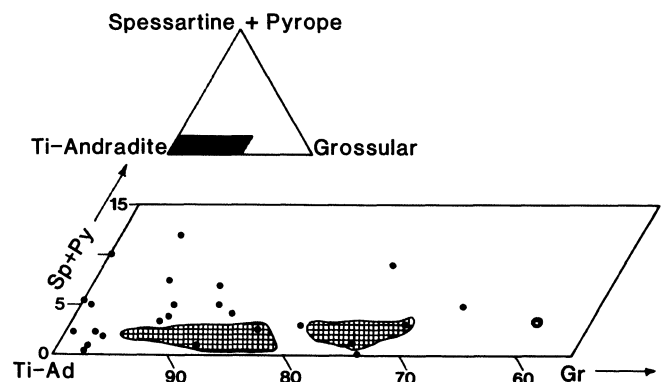


Fig. 5. Compositional range of the Crowsnest garnets (cross-hatched areas) projected into the Ti-andradite (Ti–Ad)–Grossular (Gr)–Spessartine + Pyrope (Sp+Py) system. Also shown for comparison are compositions of other Ti-rich garnets (dots) taken from Deer et al. (1982)

The compositions of the garnets from the Crowsnest volcanic rocks may also be compared to garnets from various skarn associations, recently compiled by Einaudi and Burt (1982) (Fig. 7). All skarn garnets have very low TiO₂ contents implying a much larger activity of SiO₂ during their hydrothermal formation. Apart from the difference in TiO₂ contents, however, it is clear that the Crowsnest garnets field corresponds closely to the field for Cu-skarn garnets. In contrast, the fields for Fe, W, Pb–Zn, and Sn skarns appear to be unrelated. In this regard, we note the occurrence of CuFe₂S₃ inclusions in the Crowsnest garnets and the association of metavolcanic rocks with copper porphyries in north-central British Columbia. The chemistry and mineralogy of these volcanic rocks matches very closely that of the Crowsnest volcanic rocks (Allen et al. 1976).

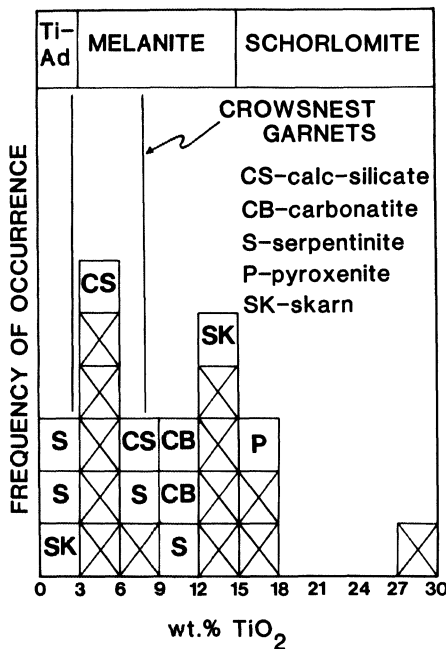


Fig. 6. Comparison of the TiO_2 content of the Crowsnest garnets and Ti-rich garnets from 24 other localities (data from Deer et al. 1982). Each locality is represented by one box. Boxes with crosses represent garnets from igneous rocks with similar chemistry to the Crowsnest volcanic rocks

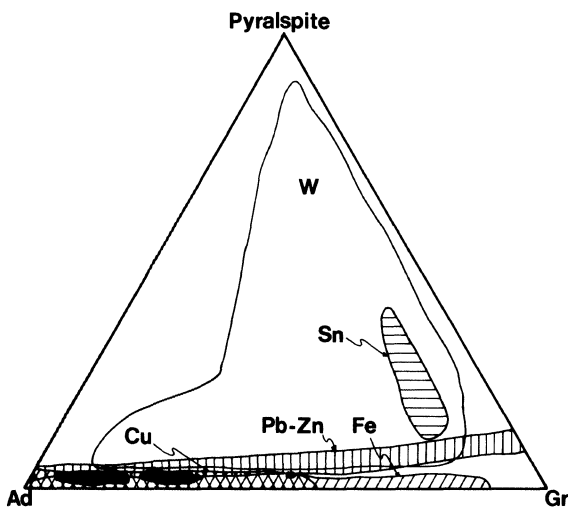


Fig. 7. Comparison of the compositional ranges of the Crowsnest garnets with garnets from various types of skarns (data from Ein-audi and Burt 1982). Ad-Andradite, Gr-Grossular, Pyralspite-Py-rope + Almandine + Spessartine. Dark areas represent compositional fields of Crowsnest garnets

Zedlitz (1933) proposed that Ti^{3+} may be present in melanite garnets and placed some of the Ti from melanite analyses into the octahedral (Y) site. At the same time, Kunitz (1936) placed Ti in tetrahedral coordination in melanite garnets. Tarte (1960) concluded from infrared spectroscopy that Ti replaces Si in the melanite molecule. The chemical study conducted by Howie and Woolley (1968) confirmed Tarte's (1960) conclusion that Ti substitutes for Si, but they suggested that Fe may be coupled with this Si-Ti substitution. In contrast, Lehijärvi (1966) and Isaacs (1968) independently argued, based on microprobe scans

and wet chemistry, that Fe-Ti is the principal exchange in these garnets.

Dowty (1971) proposed the tetrahedral site preference $\text{Fe}^{3+} > \text{Ti}$ based on Mössbauer spectra of melanites. Hartman (1969) and Huggins et al. (1977a) further proposed the preference $\text{Al} \geq \text{Fe}^{3+} > \text{Ti}$ for the tetrahedral site in a variety of synthetic melanites based on crystal chemical and Mössbauer evidence, respectively. Huggins et al. (1977a) also pointed out that melanites synthesized from gels and those occurring in serpentinized peridotites contain distinctly different ferric iron distributions than melanites synthesized from glasses and that site equilibration required several weeks at temperatures $> 1200^\circ \text{C}$. Huggins et al. (1977b), however, proposed that the dominant substitution of Ti in all but one natural melanite investigated, is the simple Si-Ti exchange.

Our work shows that all Ti cannot be accommodated in the tetrahedral site of these garnets by substitution for Si (Table 1). Therefore, some Ti must be incorporated in the octahedral site. The results of our study support the conclusion of Huggins et al. (1977b) that the dominant exchange involving Ti in these garnets is a binary Si-Ti exchange (Table 3, factor 2). We realize, however, that the Si-Ti exchange factor could be produced by an Al-conservative exchange in which the Ti in the octahedral site forces a proportion of Al into the tetrahedral site with Si to maintain charge balance. Otherwise, significant coupling of Al or Fe in this exchange is ruled out by the absence of significant factor loadings in the Si-Ti exchange factor (Table 3). In addition, the absence of a strong factor loading for Ti in the Al-Fe factor (Table 3, factor 1) suggests that Ti (octahedral or tetrahedral) is relatively insensitive to variations in Fe and Al content.

We have no direct information on the valence of Ti in these garnets. However, the dominance of the Si-Ti exchange (without Al or Fe coupling) in accounting for the variations in Si and Ti content of these garnets implies that the Ti is dominantly tetravalent. Also, we note from Table 1 that the wet chemical determinations of the reduced cations satisfy very well the charge balance of the garnet molecule if all Ti is assumed to be tetravalent. It appears logical to us to assign this reduced cation value to ferrous iron which is used to balance the presence of a tetravalent Ti in the octahedral site rather than assigning the reduced cation value to Ti (i.e. Ti^{3+}). We also realize that a small amount of H_2O may be present in the Ti-andradite structure (e.g. Onuki et al. 1982), which would have little effect on the total obtained by microprobe analysis. The addition of H_2O by the hydrogarnet substitution 4H^+ for Si^{4+} , however, would have a large effect on the oxygen fugacity and hence the valence state of Fe and Ti.

Conclusion

We have described the chemical composition and zonation of melanite garnets occurring in alkaline undersaturated igneous rocks of the Crowsnest Formation, S.W. Alberta, Canada. The chemical variation in these garnets is dominated by binary exchanges, namely; $\text{Al}-\text{Fe}^{3+}$, $\text{Si}-\text{Ti}$, $\text{Ca}-\text{Mn}$ and $\text{Mg}-\text{Fe}^{2+}$. Although microprobe analyses can not distinguish the valence state of elements, it is inferred from the Si-Ti exchange factor that Ti^{4+} is present in the tetrahedral site. Excess Ti is assigned to the octahedral site and may be either tetravalent or trivalent. The

analyses of garnets may be cast as garnet molecules based on eight cations using wet chemical Fe determinations and assuming all Ti is tetravalent. Such molecules yield stoichiometric values of oxygen within ± 0.05 formula units. This strongly suggests that the Ti in these garnets is dominantly tetravalent. The compositional range of these garnets spans the range of investigated compositions from other localities in terms of Ca, Mn, Mg and Fe (i.e. the relative proportions of grossular, Ti-andradite and spessartine + pyrope). Their Ti content is similar to the levels commonly achieved in Ti-andradite garnets of alkaline undersaturated igneous rocks, both volcanic and plutonic.

Quantitative modelling of the origin of chemical zonation in melanite garnets from alkaline undersaturated igneous rocks should concentrate on the simulation of the four chemical exchanges we have discussed. It is these chemical variations which may provide insight into variations in the intensive parameters governing crystal-melt equilibria in these complex magmas.

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