Canadian Mineralogist
Vol. 21, pp. 529-544 (1983)

THE FORMATION OF SUBCALCIC GARNET IN SCHEELITE-BEARING SKARNS

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ABSTRACT

Compositions of garnet from 18 tungsten-bearing skarns in the western Cordillera of North America, with additional examples from the literature, indicate that solid solution between grandite and pyralspite is far more extensive than previously reported; garnet with up to 75 mole % andradite component can contain significant almandine - spessartine ("subcalcic") component. Detailed microprobe analyses show that skarn garnets are typically zoned toward more subcalcic compositions from core to rim and from periphery of skarn toward the inferred fluid-source. Among tungsten skarns, those that possess subcalcic garnet are more abundant, they generally possess higher tungsten grades and tonnages, and they appear to be more typical of occurrences in the Cordillera. A model for the occurrence of subcalcic garnet in a skarn requires relatively low oxidation-state, high manganese-ion activity, and low calcium-ion activity in skarn-forming fluids. These conditions are best met in skarns formed at moderate depths, in highly carbonaceous host-rocks and in zones chemically isolated from calcite marble. Semiquantitative calculations suggest that at oxidation states approximately at or below pyrite- magnetite-pyrrhotite, changes in activity of calcium hydroxide in solution by a factor of 2 can produce the observed compositional variations. Subcalcic garnet generally is characteristic of tungsten skarns because such skarns are typically found associated with relatively reduced plutons or wallrocks or found at relatively great depths.

Keywords: garnet, skarn, scheelite, tungsten, mineral deposits, metasomatism.

SOMMAIRE

La composition du grenat dans dix-huit skarns à tungstène de la cordillère Ouest de l'Amérique du Nord, ainsi que dans les exemples pris dans la littérature, montre que la solution entre grandite et pyralspite est de beaucoup plus étendue qu'on ne le croyait auparavant. Un grenat qui contient jusqu'à 75% du pôle andradite (base molaire) peut contenir une proportion appréciable d'une composante "subcalcique" à almandin + spessartine. Des mesures détaillées à la microsonde montrent que le grenat des skarns est généralement zoné, avec un enrichissement en termes subcalciques du coeur vers la bordure d'un cristal et des limites du skarn vers la source de la phase fluide (établie par inférence). Les skarns à tungstène qui contiennent un grenat subcalcique sont plus répandus et plus typiques dans la cordillère, et ils possèdent des teneurs et des réserves en tungstène supérieures aux exemples sans grenat subcalcique. Pour trouver un tel grenat dans un skarn, il faut un milieu relativement réducteur, et une activité élevée de l'ion Mn et réduite de l'ion Ca dans les fluides responsables. Ces conditions seraient le mieux satisfaites dans les skarns formés à profondeur intermédiaire, dans les roches-hôtes enrichies en matière organique et dans des zones isolées chimiquement des marbres à calcite. Des calculs d'ordre semiquantitatif montrent qu'à un niveau d'oxydation défini par l'assemblage pyrite - magnétite - pyrrhotine, ou même inférieur à ce niveau, un changement d'un facteur de deux dans l'activité de l'hydroxyde de calcium en solution peut expliquer les variations de composition observées. Un grenat subcalcique est caractéristique des skarns à tungstène parce que de tels skarns sont typiquement associés à des plutons ou roches encaissantes relativement réduits ou formés à grande profondeur.

(Traduit par la Rédaction)

Mots-clés: grenat, skarn, schéelite, tungstène, gîtes minéraux, métasomatisme.

INTRODUCTION

Garnet from tungsten-bearing skarns in Japan (Shimazaki 1977) covers much of the range in composition between grossularite and almandine - spessartine, with reported compositions limited to andradite contents of less than 15 mole %, and typically less than 5 mole %. Based on these data, Shimazaki (1977) concluded that "the lack of Fe^{3+} is essential for the formation of Fe^{2+} and/or Mn^{2+}-bearing grossular under low temperature and low pressure conditions." Similar occurrences of garnet with appreciable pyralspite and low andradite contents are reported from the tungsten skarns at Victory mine, Nevada (Lee 1962), the MacMillan Pass deposit, Yukon Territory (Dick 1976), the Canada Tungsten, Baker and Lened deposits, Northwest Territories (Dick 1980), the Costabonne deposit, France (Guy 1980), and Dchenitschke, central Asia Němec 1967). From similar data, Zharikov (1970) and Shimazaki (1977) concluded that the chemical environment favorable for scheelite deposition is limited to one in which ferrous-iron-bearing grossular is stable. Zharikov (1970) interpreted this to require acidic skarn-forming fluids, whereas Shimazaki (1977) suggested, instead, highly reduced environments characterized by oxidation states below the pyrrhotite - pyrite - magnetite buffer.

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In contrast with the above studies, investigations of the tungsten-bearing skarns at Lost Creek, Montana (Collins 1977), King Island, Tasmania (Kwak & Tan 1981) and the Osgood Mountains, Nevada (Taylor 1976) showed that only grandite garnet is present. Reconnaissance studies of garnet compositions from the Pine Creek mine, California (Wright 1973) and from the Black Rock mine, California (Elliot 1971), on the other hand, indicated the presence of andraditic garnet with significant almandine + spessartine component. These data show that there is a broad range of garnet compositions in tungsten skarns, that a significant almandine–spessartine component is not restricted to the grossularitic end of the grandite series, and that some tungsten skarns lack subcalcic garnet.

This paper summarizes an investigation into the environments of tungsten-skarn formation, with particular emphasis on the occurrence and compositions of subcalcic garnet and its relationship to scheelite deposition. It is based on a detailed study of tungsten skarns in the Sierra Nevada area of California (Newberry 1980), with additional data and examples from Idaho, Nevada, Montana, Yukon Territory and Northwest Territories. In this paper, the term subcalcic garnet identifies a skarn garnet that contains more than 5 mole % almandine + spessartine component.

ANALYTICAL PROCEDURES

Approximately 60 polished thin sections representing 14 skarns were analyzed using an ARL AMX electron microprobe at Queen's University, Kingston, Ontario. Major elements were determined by energy dispersion using standards whose energy spectra had been previously stored on magnetic tape, and employing an accelerating potential of 15kV, a beam current of 100–120 μA, a sample current of 0.034 μA, a beam diameter of 2-4 μm and a counting interval of 120 seconds. Raw data for the elements were initially corrected on an Ns–880 minicomputer using a multiple least-squares routine. The intensity ratios were corrected for matrix effects following Bence & Albee (1968) as well as for drift using a Fortran correction program developed by P.L. Roeder (pers. comm.). Alpha factors used in the iterative correction procedure were taken from Albee & Ray (1970). Analytical accuracy was checked by analyzing garnet and feldspar standards during each session.

An additional 43 samples were prepared as grain mounts and analyzed on an 8-channel ARL electron microprobe at the University of California, Berkeley. Samples were analyzed using a 15 kV filament voltage, a sample current of 0.2–0.3 μA, beam diameter of 2 μm, and a counting time of 50 seconds. Standards employed included grains of well-characterized garnet, pyroxene, rhodonite, anorthite, hematite and chromite. Raw data were corrected for drift; intensity ratios were corrected for matrix effects following Bence & Albee (1968) using a Fortran program developed by M.L. Rivers (pers. comm.). Several garnet samples analyzed at both laboratories yielded negligible differences in composition.

TABLE 1. REPRESENTATIVE COMPOSITIONS OF SUBCALCIC GARNET

No.	1a (core)	1b (rim)	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Weight %																
SiO_2	36.12	36.82	36.67	36.73	37.20	36.35	36.37	37.88	36.83	36.94	38.36	37.60	37.48	38.48	37.12	37.56
TiO_2	0.19	0.20	0.35	0.16	0.00	0.16	0.55	0.49	0.12	0.18	0.17	0.00	0.45	0.39	0.36	0.37
Al_2O_3	14.67	19.60	9.19	17.36	18.92	15.10	6.42	19.38	4.56	21.51	18.56	21.75	18.81	18.18	19.04	20.13
Cr_2O_3	0.15	0.13	0.23	0.00	0.00	0.05	0.36	0.04	0.13	0.25	0.27	0.00	0.12	0.27	0.11	0.14
FeO*	17.61	16.19	18.68	14.28	16.21	14.94	22.71	9.40	24.56	16.72	7.33	12.87	13.88	7.02	6.92	13.86
MnO	12.76	18.48	3.82	19.39	16.36	13.17	3.98	9.50	2.26	4.49	2.35	6.60	10.62	3.79	3.30	3.95
MgO	0.31	0.86	0.20	0.46	0.29	0.35	0.31	0.39	0.09	0.19	0.16	0.35	0.31	0.40	0.06	0.18
CaO	16.23	9.48	30.51	11.94	11.07	19.47	28.57	23.42	31.89	20.19	32.86	19.19	19.14	32.00	31.53	22.86
TOTAL	98.02	101.77	99.65	100.32	100.05	99.59	99.26	100.50	100.42	100.48	100.06	98.34	100.81	100.53	98.55	98.87
Mole % garnet end-members																
Gr	17.8	14.6	27.8	14.4	21.7	24.1	14.1	51.7	12.2	49.7	71.6	54.7	37.5	67.0	71.3	57.8
Ad	29.6	11.4	59.0	20.0	10.0	31.8	67.8	13.4	79.3	6.1	17.8	0.4	16.3	20.1	12.9	4.6
Sp	29.7	40.6	8.7	44.7	37.2	30.0	9.1	20.9	5.2	9.9	5.1	15.0	23.9	8.2	8.0	8.8
Alm	21.2	29.6	3.1	19.0	29.7	12.7	6.3	12.5	2.6	32.8	4.1	28.5	20.7	2.3	7.2	27.7
Py	1.2	3.3	0.8	1.9	1.1	1.4	1.2	1.5	0.3	0.7	0.6	1.4	1.2	1.5	0.2	0.7
Uv	0.4	0.4	0.7	0.0	0.0	0.1	1.1	0.1	0.4	0.8	0.8	0.0	0.4	0.8	0.4	0.4

*Total iron as FeO; Gr = grossularite, Ad = andradite, Sp = spessartine, Alm = almandine, Py = pyrope, Uv = uvarovite
Nos. 1,2: Pine creek mine, 1189 1st sublevel drift, 1 = .6 m from intrusion, 2 = 6 m from intrusion; 3-5: Black Rock mine, 3 = 711 stope, 6700 level, 4 = 833 stope, 6600 level, 5 = 711 drift, 6700 level; 6,7: Strawberry mine, 6 = vein garnet from outcrop of #7 mine, 7 = garnet near quartz monzonite dike, K lens, 2nd level, #1 mine; 8: outcrop of alpine mine, 7 m from intrusion, subcalcic rim; 9-11: outcrop of Garnet Dike mine, 8 = Long Ridge area, garnet vein in skarn 2 m from intrusion, 9 = upper workings area, skarn adjacent to pegmatite dike, 10 = lower workings area, near endoskarn contact; 12,13: Hardpoint mine, 12 = DDH HP-11 157.5', garnet vein in skarn 3 m from dike contact, 13 = outcrop near portal, garnet vein in skarn; 14: outcrop of Tungsten Jim mine, massive garnet skarn 2 m from intrusion; 15: Lened prospect, Cac Valley area, 3 m from intrusion. Skarn locations shown on Figure 1.

Calculation of molecular end-members was made following Rickwood (1968) after assignment of ferric and ferrous iron. Ferric iron was determined by subtracting the amount necessary to complete trivalent occupancy from total iron per 24 oxygen atoms; the remaining iron was assumed to be ferrous. The analysis was rejected as unsatisfactory if the cation total (ferrous iron + manganese + calcium) differed from 6.00 (per 24 oxygen atoms) by more than 2%. Typical subcalcic garnet compositions are listed in Table 1.

Geology and Geochemistry of Subcalcic Garnet Occurrences

Geology of subcalcic garnet occurrences in skarns of the North American Cordillera

Most of the hundreds of tungsten-bearing skarns in the Western Cordillera of Canada and the United States are located at or near contacts between calcareous metasedimentary rocks and coarse-grained calcalkaline plutons of Triassic to Cretaceous age. The locations of tungsten-bearing skarns discussed in this paper are shown in Figure 1. Of the thirty occurrences shown, all but seven contain subcalcic garnet. In all cases, subcalcic garnet ± quartz forms an assemblage with a consistent paragenetic setting, proximal to the intrusive contact. The detailed occurrence of subcalcic garnet and space–time variations in its composition vary with the type of host rock.

Tungsten-bearing skarns exist in host rocks ranging from pure marble to calcareous hornfels, and from massive units to thinly intercalated or diamictitic units. These different host-rocks impart characteristic morphologies and patterns of zonation upon the skarns. Wallrocks also vary from extremely carbonaceous to noncarbonaceous or even hematitic,

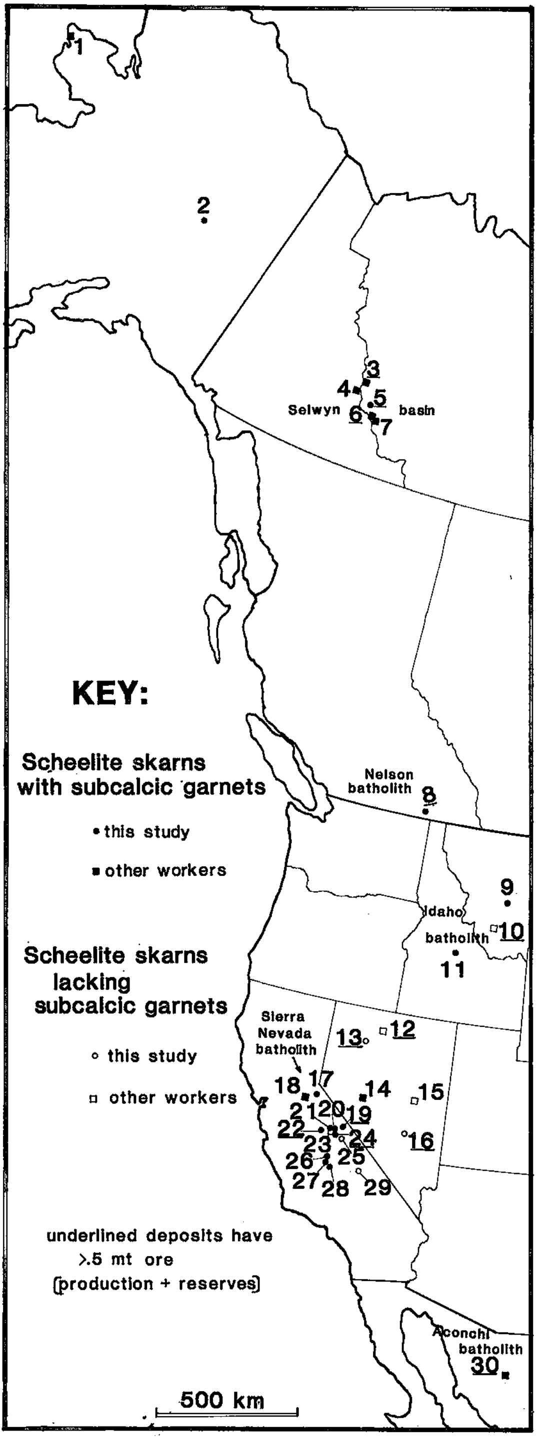

FIG. 1. Location of tungsten-bearing skarns of the western North American Cordillera discussed in this paper. Skarns with subcalcic garnet indicated by closed symbols; skarns lacking subcalcic garnet indicated by open symbols. Deposits: 1) Lost River, Ak. (Dobson 1982); 2) Spruce Hen prospect, Fairbanks district, Ak.; 3) Macmillan Pass, Yukon–Northwest Territories (Dick 1976); 4) Clea, Yukon (Dick 1980); 5) Lened, N.W.T. (Dick 1980, this study); 6) Canada Tungsten, N.W.T. (Dick 1980); 7) Baker, N.W.T. (Dick 1980); 8) Emerald, B.C.; 9) Colorado Gulch, Mont.; 10) Lost Creek/Brown's Lake, Mont. (Collins 1977); 11) Tungsten Jim, Id.; 12) Osgood Mountains, Nv. (Taylor 1976); 13) Mill City, Nv.; 14) Victory mine, Nv. (Lee 1962); 15) Monte Cristo, Nv. (Sonnevil 1979); 16) Emerson, Nv.; 17) Alpine, Ca.; 18) Garnet Hill, Ca. (Brock 1970); 19) Black Rock, Ca.; 20) Hilton Creek, Ca.; 21) Hardpoint, Ca.; 22) Strawberry, Ca. (this study, Nokleberg 1981); 23) Scheelore, Ca. (Morgan 1975); 24) Pine Creek, Ca. (this study, Brown 1980); 25) Tungsten Hills, Ca.; 26) Garnet Dike, Ca.; 27) Consolidated, Ca.; 28) Tulare Co., Ca.; 29) Darwin, Ca. (this study, Eastman 1979); 30) El Jaralito, Sonora, Mexico (Peabody 1979, Dunn 1980).

TABLE 2. CONTRASTING CHARACTERISTICS OF REDUCED AND OXIDIZED TUNGSTEN SKARNS

	Reduced Skarns		Oxidized Skarns
Characteristic	Strongly reduced	Moderately reduced	
host rocks	strongly carbonaceous (>5% carbon common)	moderately carbonaceous (0.5 to 2% carbon typical)	non-carbonaceous or hematitic
associated plutonic rocks	ilmenite or magnetite bearing	magnetite bearing	magnetite bearing
endoskarn mineralogy	pyroxene-plagioclase ± quartz	pyroxene-plagioclase ± quartz-epidote	quartz-epidote ± plagioclase
skarn mineralogy			
prograde assemblages			
pyroxene/garnet ratio	10:1 to 2:1	2:1 to 1:2	1:2 to 1:10
pyroxene composition*			
mole % hedenbergite	60-90	50-70	20-45
mole % johannsenite	0 -10	10-25	0- 5
garnet composition			
mole % andradite	10-30	30-75	50-80
late garnet composition			
mole % andradite	0-30	10-75	80-98
mole % spessartine	3-35	5-40	0- 3
mole % almandine	3-40	2-35	0
retrograde assemblages			
typical mineralogy (± quartz, calcite)	biotite, plagioclase hornblende, opaques	biotite, hornblende, chlorite, opaques	epidote, chlorite, actinolite, opaques
amphibole composition			
mole % ferrotremolite	0-50	5-60	30-60
mole % tremolite	0-10	10-40	30-70
mole % pargasite	50-98	5-70	5-20
diagnostic opaques	pyrrhotite (Bismuth)	pyrite-magnetite-pyrrhotite	pyrite ± magnetite (bismuthinite)
examples	Hardpoint, Ca MacMillan Pass, YT Canada Tungsten, NWT Tungsten Jim, Id.	Pine Creek, Ca. Black Rock, Ca. El Jaralito, Mexico Colorado Gulch, Mont.	Osgood Mntns., Nv. Lost Creek, Mont. Tungsten Hills, Ca.

*remainder is diopside; **remainder is grossularite

indicating that the oxidation state of host rocks can be highly variable (Newberry 1980).

Compositions of skarn-mineral assemblages, compositions, and local geological settings indicate that tungsten skarns can be classified into three categories: "strongly reduced", "moderately reduced " and "oxidized". Characteristics of these three types are listed in Table 2, adapted from Einaudi *et al.* (1981). Reduced skarns, characterized by ferrous-iron-rich minerals, are found in carbonaceous host rocks or associated with reduced plutons (crystallized at depth or ilmenite-bearing, or both). Oxidized skarns, characterized by ferric-iron-rich minerals, are found in noncarbonaceous or hematitic host rocks or associated with oxidized plutons (crystallized at shallow depths or magnetite-bearing, or both). Subcalcic garnet has only been identified in the reduced skarns; andradite and epidote–quartz are the paragenetically equivalent assemblages in oxidized skarns.

Most tungsten-bearing skarns show either simple or complex mineralogical zonation depending on the host lithology. Skarns formed from relatively pure, thick marble beds, (*e.g.*, the Canada Tungsten mine, N.W.T., and the Pine Creek, Hilton Creek, and Garnet Dike mines, Ca.), are characterized by mineralogically simple time-equivalent metasomatic zones containing mineral assemblages with increasing calcium contents progressing from the intrusive contact toward marble. In these simple cases, zones containing subcalcic garnet ± quartz are at the centre of skarn veins and closest to intrusive contacts, in contact with and replacing salitic pyroxene – grandite garnet skarn. Zones of subcalcic garnet contain variable amounts of quartz, typically between 5 and 80%, but on average about 30%. They contain no scheelite (Newberry & Einaudi 1981) and form a sharp cut-off in grade adjacent to ore-bearing garnet–pyroxene skarn.

Veins of subcalcic garnet ± quartz commonly extend outward from massive garnet–quartz, replacing garnet–pyroxene skarns several metres from the contact (Fig. 2). Garnet compositions vary systematically within these veins, becoming less subcalcic with distance into the garnet–pyroxene skarn (Fig. 2) and eventually approach the composition of the wallrock grandite. Grains of subcalcic garnet within the garnet–quartz zone may be slightly zoned, becoming 5 to 20 mole % more subcalcic from core to rim (Table 1).

Skarns formed from heterogeneous carbonate lithologies do not show the well-developed outcrop-scale zoning characteristics of skarns formed from thick marble beds, except that a subcalcic garnet ± quartz zone may be directly adjacent to the pluton. Calc-silicate grains and layers formed by metamorphic recrystallization are typically overprinted by

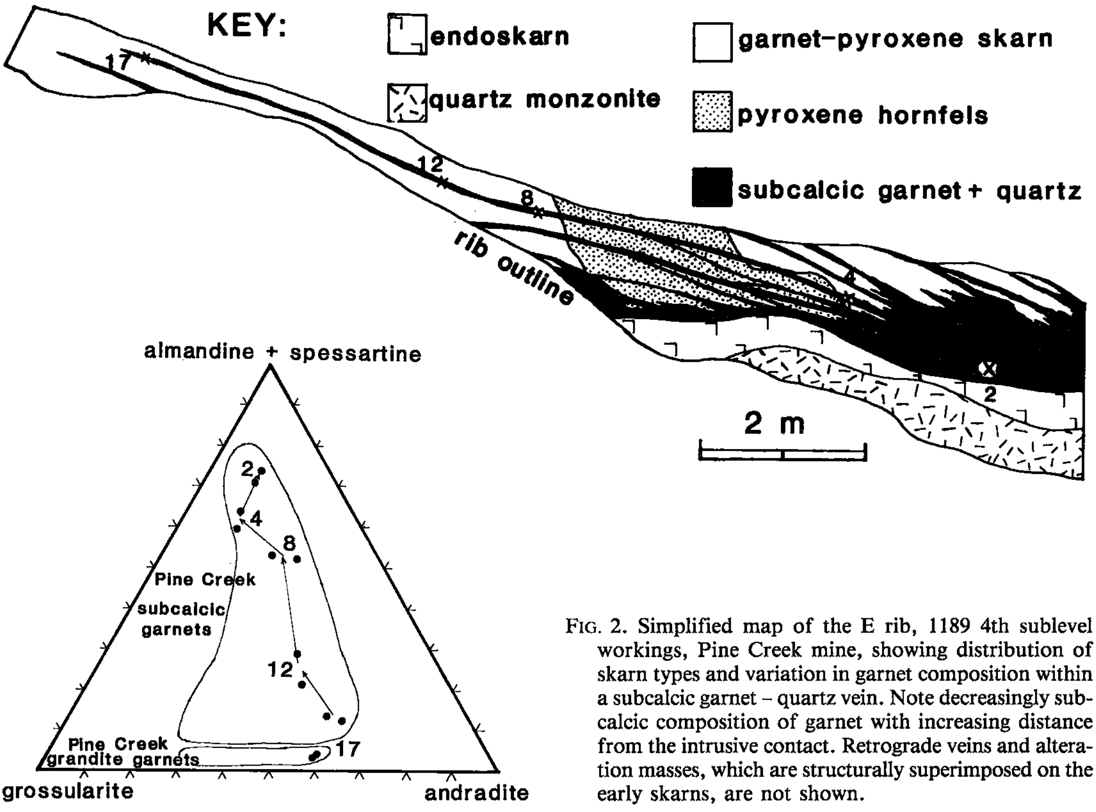

FIG. 2. Simplified map of the E rib, 1189 4th sublevel workings, Pine Creek mine, showing distribution of skarn types and variation in garnet composition within a subcalcic garnet – quartz vein. Note decreasingly subcalcic composition of garnet with increasing distance from the intrusive contact. Retrograde veins and alteration masses, which are structurally superimposed on the early skarns, are not shown.

metasomatic calc-silicates; individual garnet grains are typically zoned, in most cases with grossularitic or granditic cores and increasingly subcalcic rims (Figs. 3, 4). Subcalcic garnet typically coats the inside of vugs formed by coalescing grains of grandite garnet (Fig. 5). Subcalcic garnet grains also occur as late, discontinuous veins in garnet–pyroxene skarn and hornfels, and are not present in marble or other high-calcium rocks. Where subcalcic garnet occurs adjacent to calcite, the calcite is always a late, vug-filling mineral (Fig. 3). These textures suggest that subcalcic garnet did not form in a given spot until the calcite originally present was entirely dissolved by metasomatic fluids.

Zonation in garnet compositions also occurs on the scale of hundreds of metres (*e.g.*, the Black Rock mine, Fig. 6). The maximum amount of subcalcic component present in garnet at Black Rock varies from more than 80% near the quartz monzonite contact to less than 10% in skarn exposed about 250 metres from the contact. At the Strawberry and Hardpoint skarns the maximum subcalcic contents are found in garnet adjacent to quartz monzonite stocks and dykes; the sparse data suggest a decrease in the subcalcic component with distance from the intrusive body. At Black Rock, garnet compositions are not a simple function of distance from the intrusive body, but rather reflect the latest paths of fluid flow controlled by sedimentary layering.

Most known oxidized skarns formed from inhomogeneous carbonate lithologies [*e.g.*, King Island, Aust.: Edwards *et al.* (1956)], so that their zoning sequences are difficult to decipher. In several cases [Osgood Mountains, Nevada: Taylor (1976), Tungsten Hills, California: Newberry (1980), Lost Creek, Montana: Collins (1977)], however, the sequence appears to be: a narrow outer wollastonite-idocrase zone, a thick main zone of andraditic garnet ± salitic pyroxene, and an inner epidote–quartz zone of variable width adjacent to the intrusive body. Garnet grains within the garnet ± pyroxene zone of oxidized skarns are typically zoned from a grossularitic core to a nearly pure andradite rim (Taylor 1976, Collins 1977).

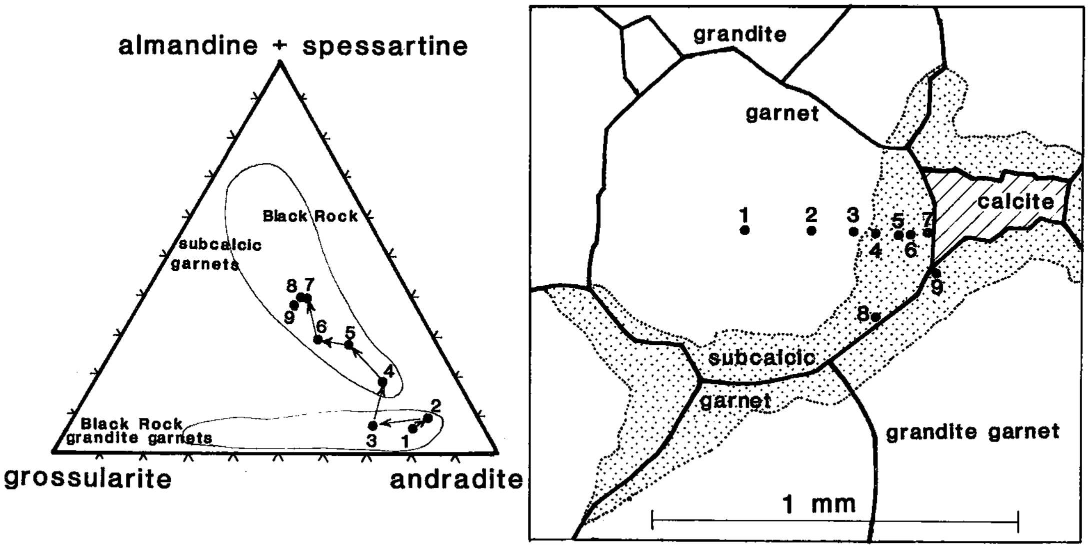

FIG. 3. Sketch from a thin section of skarn from the 831 stope, 6600 level, Black Rock mine, showing compositional zoning and development of subcalcic rim on grandite garnet. Subcalcic garnet areas are indentified in thin section by pale orange color in transmitted light and anomalous birefringence with crossed polarizers. Note pattern of zoning of increasingly subcalcic garnet compositions toward rim. Late calcite – chlorite veinlets not shown.

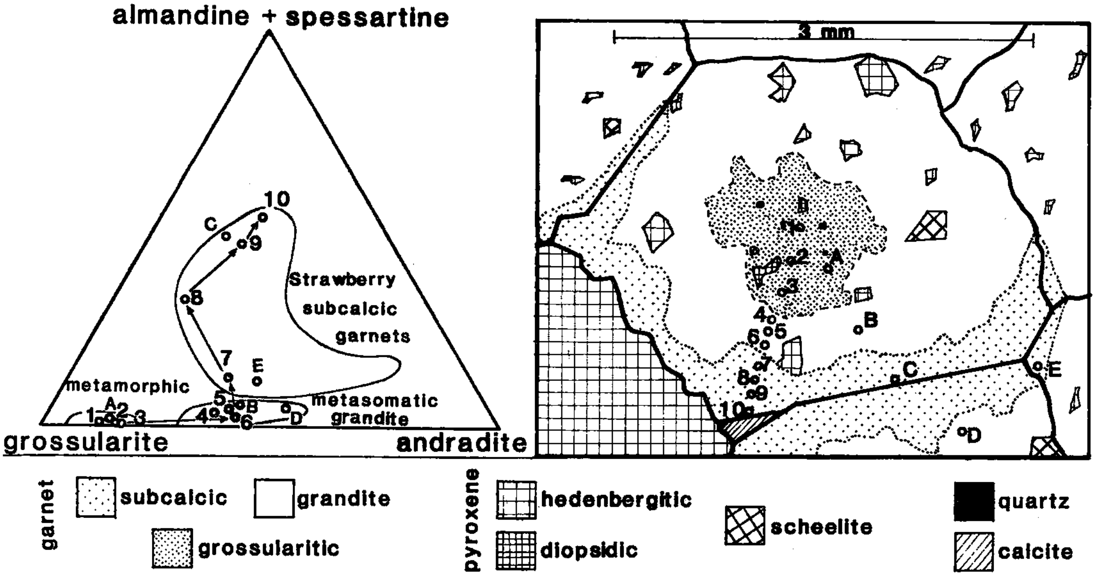

FIG. 4. Sketch of thin section from No. 2 orebody pit, Strawberry tungsten mine. Metamorphic grossularitic core with quartz and diopside inclusions is surrounded by metasomatic grandite with scheelite and hedenbergitic pyroxene inclusions, in turn rimmed by subcalcic garnet. Vug is filled with late, clear calcite. Garnet compositions become more subcalcic toward rim. Garnet types are indicated by color differences in transmitted light and crossed polarizers.

Bulk-composition relationships in subcalcic garnet

Compositions of subcalcic garnet determined in this study are plotted in terms of mole % grossularite, andradite, and almandine + spessartine components in Figure 7. The plot clearly indicates the wide range in solid solution between grandite and pyralspite found in these occurrences. Almandine–spessartine substitution is clearly not limited to very andradite-poor compositions: a garnet with as much as 75 mole % andradite can contain appreciable almandine + spessartine. Garnet compositions recorded from strongly reduced skarns, similar to those reported by Shimazaki (1977), form a subgroup characterized by low andradite and high grossularite contents. Garnet compositions recorded from moderately reduced skarns form a compositionally distinct group with a higher andradite content. The contrast in compositions between the two groups of reduced skarns is further illustrated in terms of relative almandine and total iron components (Fig. 8). In the moderately reduced skarns, total-iron contents are approximately independent of almandine content, whereas the strongly reduced skarns show a linear increase in iron content with increase in almandine content. The former trend reflects an approximately fixed amount of total iron in garnet, distributed between ferrous and ferric forms, rather than a fixed ratio of ferrous to ferric iron.

Differences in relative almandine/spessartine ratios also help to differentiate between the two types of skarn (Table 1). Strongly reduced skarns are characterized by high almandine/spessartine ratios (1:1 to 4:1), whereas moderately reduced skarns have low ratios (1:1 to 1:5, averaging about 1:2). These differences are addressed in a subsequent section.

Compositional differences between the two groups are summarized in a plot of the molar ratios andradite/grossularite *versus* almandine/spessartine (Fig. 9). Strongly reduced skarns are characterized by low andradite/grossular and variable, but generally high almandine/spessartine ratios, whereas moderately reduced skarns possess relatively high andradite and low almandine. Subcalcic garnet compositions from Japanese tungsten skarns (Shimazaki 1977) show similar trends, but with lower overall iron contents. The strongly antithetic relationship observed between almandine/spessartine and andradite/grossularite ratios suggests a causal relationship between the two ratios and merits further consideration. Clearly, if garnet compositions are uniquely fixed by a buffered $f(O_2)$, then almandine–andradite ratios should not show this strong inverse correlation. Other factors besides oxidation state must be important.

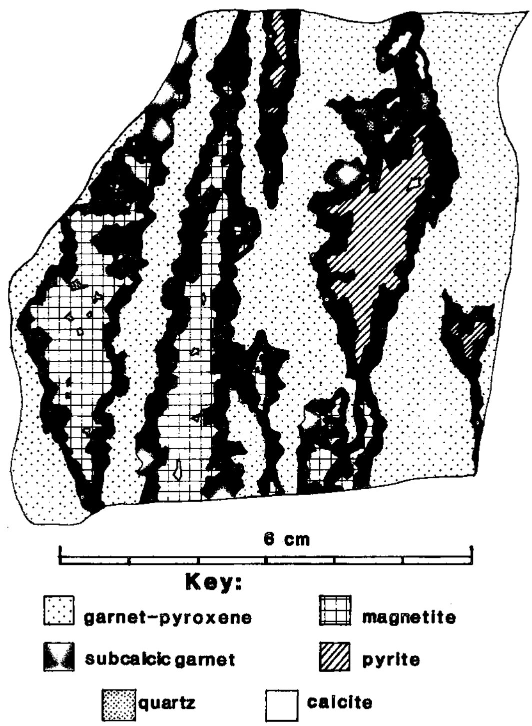

FIG. 5. Sketch of an unusually subcalcic-garnet-rich hand specimen from the 711 stope, 6700 level, Black Rock mine, showing the complexity of the mineral zonation present. The skarn protolith consisted of interlayered marble and calc-silicate hornfels beds; replacement of the marble interbeds from contacts with hornfels resulted in the formation of garnet–pyroxene skarn followed by subcalcic garnet. Vugs were filled with pyrite, pyrrhotite, magnetite, quartz and calcite during later retrograde alteration.

DISCUSSION

Oxidation state and stability of subcalcic garnet

The oxidation state present during early stages of skarn formation may be estimated by using experimentally derived mineral-asssemblage buffers appropriate for calcic garnet–pyroxene assemblages adjusted for mineral composition. Results of such calculations (Newberry 1980, Einaudi *et al.* 1981) demonstrate the contrast in oxidation state between skarns that lack and skarns that possess a subcalcic garnet. These workers suggested that tungsten skarns generally form at oxidation states below or only slightly exceeding the pyrrhotite – magnetite – pyrite buffer and that there is some *causal* relationship be-

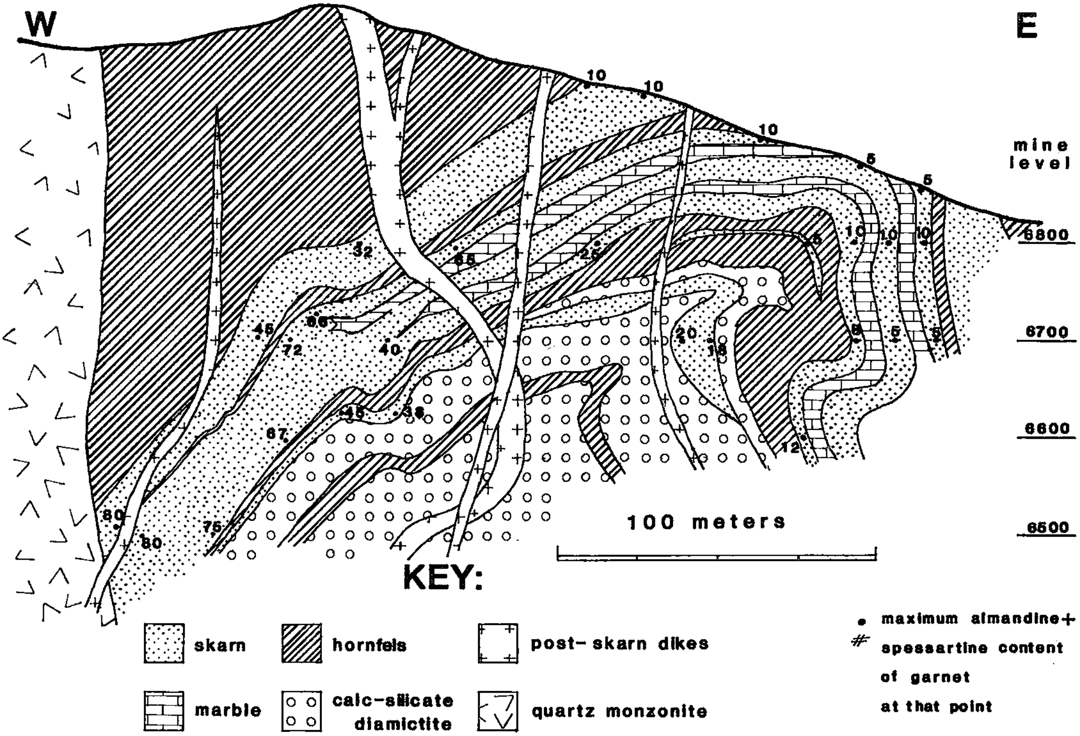

FIG. 6. Simplified geological cross-section through the Black Rock mine, showing distribution of skarn and change in garnet compositions within the mine. Numbers indicate the maximum subcalcic component in garnet at various points, projected into the line of section. Compositional data presented include values of cell dimension and index of refraction from Elliot (1971). Note systematic increase in maximum subcalcic component of garnet toward the quartz monzonite contact. Late, high-angle faults (less than 20 m displacements) have been deleted for clarity.

tween oxidation state and skarn type. For example, biotite compositions indicate that most plutons of the eastern and central Sierra Nevada cooled along a buffered path appoximately 2-3 log units above the Ni-NiO buffer (Dodge *et al.* 1969, Dodge 1972). This log $f(O_2)$ - T path corresponds to the $f(O_2)$ - T regime of moderately reduced tungsten skarns (Newberry 1980) found in the central and eastern Sierra Nevada of California. In the western United States, oxidized tungsten skarns (Fig. 1) occur east of the deeper batholith terranes (Sierra Nevada, Aconchi, Idaho, Nelson); depth-of-formation estimates for these deposits are generally less than those to the west, and oxidation states were presumably higher (Newberry & Einaudi 1981). Thus, the mineralogy of a typical tungsten skarn in part simply reflects the imposed oxidation state.

This evidence from natural assemblages is corroborated by the experimental studies of Liou (1973), who found that grandite garnet with a significant almandine component could form only at an oxidation state along or below the Ni-NiO buffer. Graphical interpretation after Winchell (1958) of data presented by Liou (1973) indicates that over the temperature range of 750 to 600°C for the assemblage anorthite-spinel-garnet-quartz, the ratio of almandine to andradite component in garnet is a function of $f(O_2)$. The restriction of subcalcic garnet to oxidation states at or below Ni-NiO in Liou's (1973) experiments, however, is not reflected in natural assemblages owing to two differences between the experimental and natural occurrences: (1) variability in the calcium content of natural mineral assemblages and (2) the presence of a substantial manganese component in the skarn-forming fluids. These effects are considered in the following paragraphs.

Calcium activity and subcalcic garnet in skarns

Subcalcic garnet compositions from moderately reduced skarns are characterized by variable Fe^{2+}/Fe^{3+} ratios, independent of total iron content (Fig. 8). Garnet compositions in these skarns become more subcalcic with proximity to the fluid source (Figs. 2, 6) and with time (Figs. 3, 4); subcalcic garnet

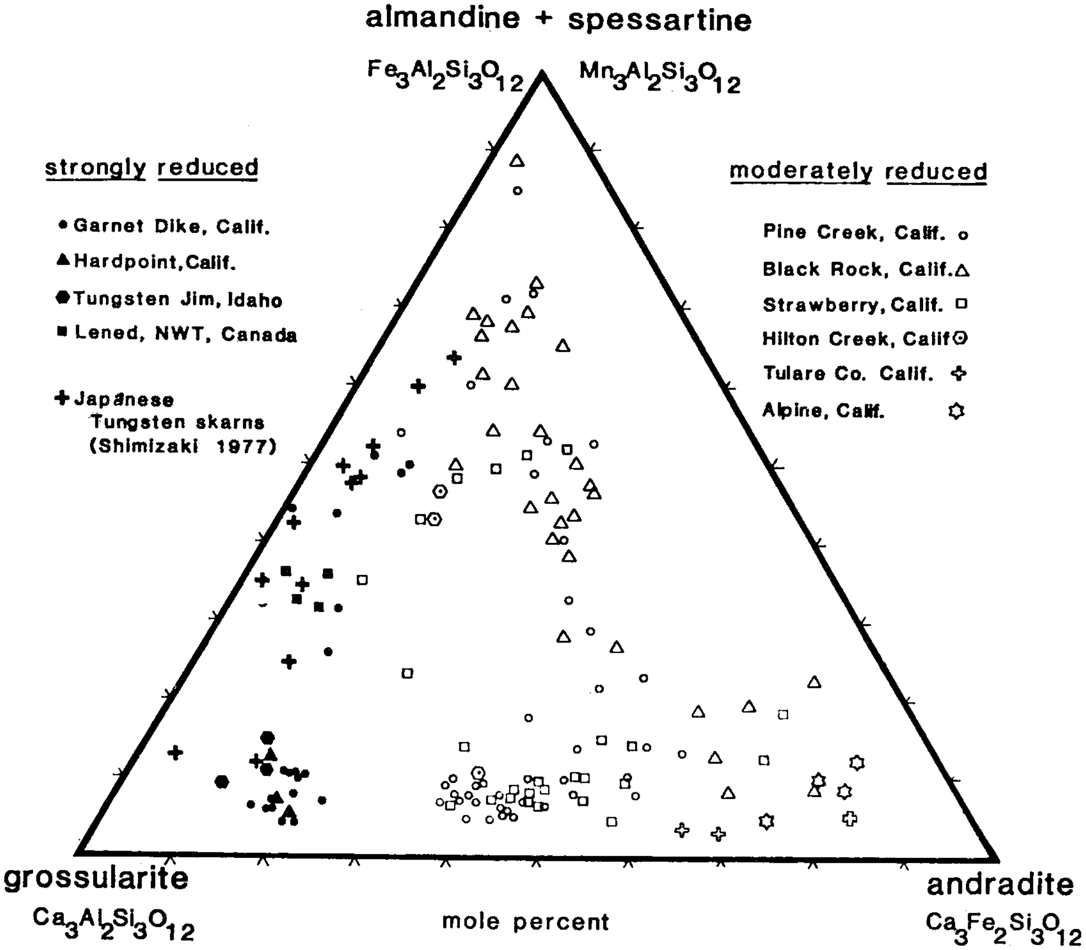

FIG. 7. Compositions of all subcalcic garnet specimens analyzed for this study, expressed in terms of mole % grossularite, andradite, and almandine + spessartine. Filled symbols represent garnet from strongly reduced skarns, open circles represent garnet from moderately reduced skarns. Note in this figure, and in Figures 8 and 9, the close similarity between strongly reduced skarns of this study and the Japanese skarns of Shimazaki (1977).

is not found as a replacement of high-calcium minerals. These facts suggest that a low calcium-ion activity is a critical prerequisite to formation of subcalcic garnet in skarns. For moderately reduced skarns, formation of subcalcic garnet from grandite skarn can be approximated by a reaction that conserves iron and aluminum:

$$\underset{\text{in garnet}}{3Ca_3Fe_2Si_3O_{12}} + \underset{\text{in garnet}}{2Ca_3Al_2Si_3O_{12}} + 15H_2O \rightleftharpoons \underset{\text{in garnet}}{2Fe_3Al_2Si_3O_{12}} + \tfrac{3}{2}O_2 + \underset{\text{quartz}}{9SiO_2} + 15Ca(OH)_2(aq) \qquad (1)$$

(owing to complexation of aqueous ions at high temperature, calcium ion is represented by a calcium hydroxide complex; depending on fluid composition, chloride, fluoride and carbonate complexes would presumably be present as well.) The equilibrium *a* constant for the reaction, assuming $a(H_2O) = a(SiO_2) = 1$, is:

$$K_{eq} = \frac{a_{alm}^{2}\, f(O_2)^{3/2}\, a_{Ca(OH)_2}^{15}}{a_{ad}^{3}\, a_{gr}^{2}} \qquad (2)$$

If oxygen fugacity, temperature and pressure are approximately constant, as might be expected during the formation of a single zoned grain of subcalcic garnet (*e.g.*, Fig. 4), then the activity of the calcium

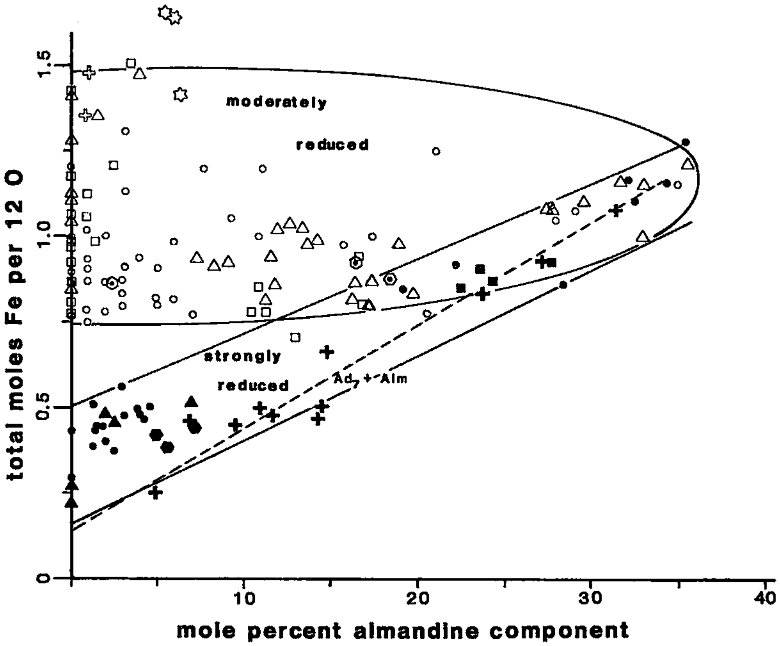

FIG. 8. Almandine content *versus* total moles iron per 12 oxygen atoms in analyzed subcalcic garnet. Garnet compositions from strongly reduced skarns show an approximately linear relation between total iron and almandine content, garnet compositions from moderately reduced skarns show approximately constant total iron content, independent of almandine content. Dashed line through points from Japanese tungsten skarns describes the equation total moles iron = 7 mole % Ad + mole % Alm.

ion in solution, as expressed by $a_{\mathrm{Ca(OH)_2}}$, ought to be directly proportional to: $a_{\mathrm{ad}}{}^3\, a_{\mathrm{gr}}{}^2 / a_{\mathrm{alm}}{}^2$ and designated *R*. The calculation of the quantity *R* is complicated by the fact that some of the components have strongly nonideal mixing properties (Ganguly 1976) and thus, non-unit activity coefficients (Ganguly & Kennedy 1974). Activity coefficients for the almandine–grossular system at 850°C vary from 0.8 to 1.8 (Cressey *et al.* 1978) and are not known below 850°C, although calculations by Saxena (1973) suggest that they may be as high as 3 or 4 at 400°C. Use of regular-solution models for derivation of pyrope–grossular solid solutions (Newton 1977) has resulted in highly divergent estimates of interaction parameters; thus a rigorous derivation of activity coefficients is not employed here. Within the accuracy of the calculated values, activity coefficients can be approximated as simple functions of the applicable mole fractions.

Because almandine and spessartine mix in a relatively ideal manner (Ganguly & Kennedy 1974), as do grossularite and andradite (Ganguly 1976), activity coefficients can be formulated in terms of the grandite and pyralspite components. Interpolation between the calculated values of Cressey *et al.* (1978) and those of Saxena (1973) yields activity coefficient *versus* mole-fraction relations that can be approximated as simple functions. These are:

$\gamma_{\mathrm{gr}} = \gamma_{\mathrm{ad}} = 1 + 3(1 - X_{\mathrm{grandite}})$ for $1 < X_{\mathrm{grandite}} > 0.4$, $\gamma_{\mathrm{alm}} = 3 - 5(1 - X_{\mathrm{grandite}})$ for $1 < X_{\mathrm{grandite}} > 0.55$, and $\gamma_{\mathrm{alm}} = 0.75$ for $0.55 < X_{\mathrm{grandite}} > 0.3$.

The relationship between garnet composition and the activity of a garnet end-member is modeled by a multisite mixing model (Wood & Nicholls 1978):

e.g., $a_{alm} = X_{\mathrm{Fe^{2+}}}{}^3\, X_{\mathrm{Al^{3+}}}{}^2\, \gamma_{\mathrm{alm}}$, thus

$$R = \frac{X_{\mathrm{Ca^{2+}}}{}^{15}\, X_{\mathrm{Fe^{3+}}}{}^{6}\, \gamma_{\mathrm{ad}}{}^3\, \gamma_{\mathrm{gr}}{}^2}{X_{\mathrm{Fe^{2+}}}{}^{6}\, \gamma_{\mathrm{alm}}{}^2} \qquad (3)$$

Values of *R* calculated from equation 3 vary from 105 to 1.8 × 10^{-8} within a single zoned grain of garnet (*e.g.*, from the Black Rock mine). If calcium-ion activity is approximately constant, then $f(\mathrm{O_2})$ must vary at a single spot by approximately 6 orders of magnitude to account for the observed almandine/andradite ratios. Such variation is exceedingly unlikely. The observed variation in R, however, can be completely accounted for by variations in the activity of calcium hydroxide by a factor of only 4.4 (equation 2). Such variations, at constant $f(O_2)$ and T, are feasible once high-calcium minerals have been completely replaced or dissolved. Calculations by Bird & Helgeson (1981), for example, indicate that grandite is stable over a 5-fold range in calcium-ion activity at 400°C and 1 kbar.

In strongly reduced skarns, subcalcic garnet ± quartz appears as a replacement of hedenbergitic pyroxene ± grossularitic garnet ± plagioclase. Compositional relationships indicate that andradite contents are roughly constant and independent of almandine content (Fig. 8). The reaction can be modeled as:

$$\underset{\text{in pyroxene}}{3\,CaFeSi_2O_6} + \underset{\text{in garnet}}{Ca_3Al_2Si_3O_{12}} + 6\,H_2O \rightleftharpoons$$

$$\underset{\text{in garnet}}{Fe_3Al_2Si_3O_{12}} + \underset{\text{quartz}}{6\,SiO_2} + 6\,Ca(OH)_2 \quad (4)$$

for which, assuming $a(H_2O) = a(SiO_2) = 1$,

$$K_{eq} = \frac{a_{alm}\, a_{Ca(OH)_2}{}^6}{a_{hd}{}^3\, a_{gr}} \quad (5)$$

Reduction of ferric iron is not required in this reaction, and it is thus independent of $f(O_2)$. Calculations using the previously described activity-coefficients indicate that within a single deposit, a variation in aqueous calcium-ion activity by a factor of 3 can account for the spectrum of grossular/almandine values observed. Similar treatment of the data of Shimazaki (1977) indicates that variations in activity of the aqueous calcium ion by a factor of 2.2 could account for his observed variations.

In summary, it is important to note that subcalcic garnet in tungsten skarns is not in equilibrium with a calcic clinopyroxene - grandite garnet - scheelite assemblage, but rather replaces that assemblage. When forming the assemblage pyroxene - garnet - scheelite, skarn-forming fluids replacing marble have sufficiently high values of activity of the calcium ion to prevent formation of a subcalcic garnet. Continued addition of a high-silica, low-calcium metasomatic fluid to a garnet - pyroxene - scheelite skarn results in the depletion of calcium in the fluid and the concomitant deposition of subcalcic garnet ± quartz (Fig. 10). Further depletion of calcium ion from the metasomatic fluid results in the formation of increasingly subcalcic garnet (Fig. 10). This same trend of decreasing calcium activity toward the fluid source in oxidized skarns results in the replacement of andraditic garnet by epidote + quartz, an assemblage with approximately the same bulk composition as subcalcic garnet ± quartz (Fig. 10), but possessing dominantly ferric, rather than ferrous, iron.

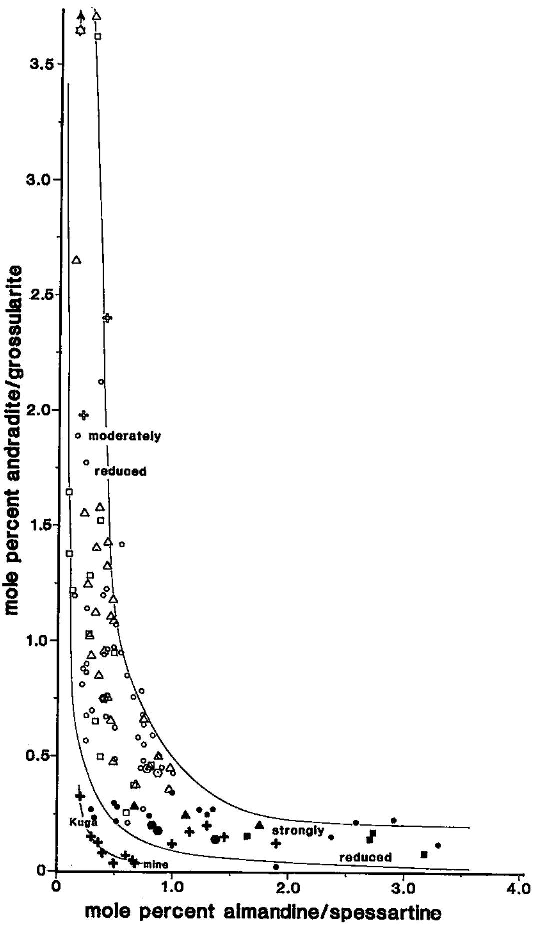

FIG. 9. Ratio of mole % almandine to mole % spessartine *versus* ratio of mole % andradite to mole % grossularite in analyzed specimens of subcalcic garnet. Note sharp distinction between moderately and strongly reduced groups and strong inverse correlation between the two ratios.

Manganese activity and subcalcic garnet in skarns

Manganese also plays a part in the observed almandine/andradite relations, as previously suggested (Fig. 9). Moderately reduced tungsten skarns are characterized by a high spessartine/almandine ratio, always greater than 1:1 and typically 2:1, whereas strongly reduced skarns are characterized by a low ratio, less than 1:1 and typically 1:2. The ratio of spessartine to almandine also increases with increasing andradite content (Fig. 9). Manganese, of intermediate size between ferrous iron and calcium,

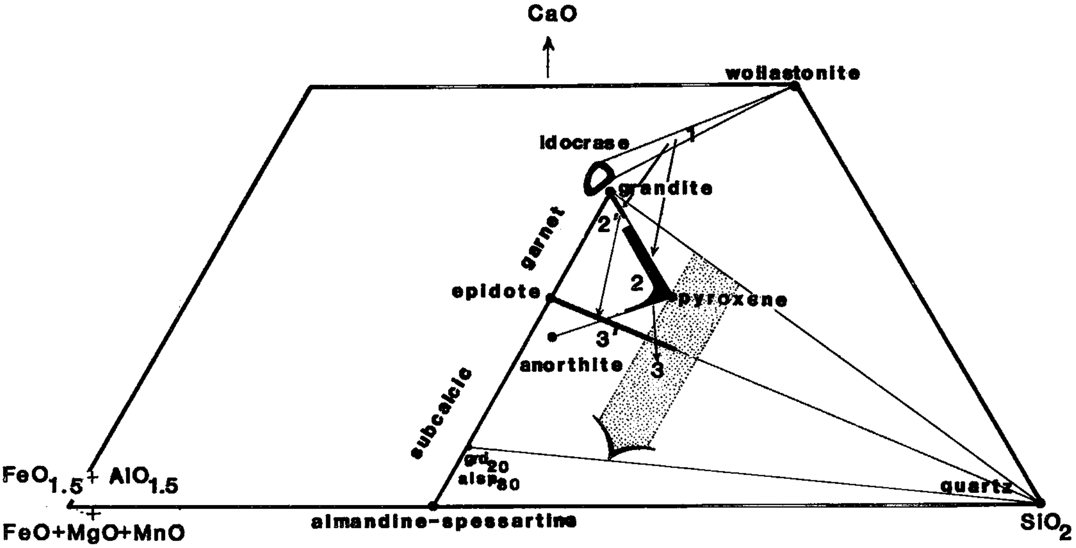

FIG. 10. Compositional triangle showing generalized compositions of mineral zones in tungsten skarns in terms of mole % CaO, SiO_2, and $FeO_{1.5}$ + $AlO_{1.5}$ + FeO + MgO + MnO. Numbers represent distinct mineral zones from marble (1) toward intrusive contact (3). Primed numbers refer to oxidized skarns, unprimed to reduced skarns. Zoning for both skarn types is from CaO-rich to increasingly CaO-poor assemblages moving away from the marble contact.

appears to play a role in the stabilization of andradite–almandine combinations. Studies of garnet-stability relations (Novak & Gibbs 1971) indicate that increasing the average cation-size in the site occupied by trivalent cations (*i.e.*, increasing the Fe^{3+} to Al^{3+} ratio) results in increasing destabilization of small cations in the divalent cation sites (*i.e.*, decreases the stability of Fe^{2+}in the garnet). Thus, in the andradite-rich garnets of moderately reduced skarns, higher manganese contents are apparently required to stabilize a given amount of ferrous iron in the garnet, and increasing the andradite/grossular ratio in garnet increases the minimum spessartine/almandine ratio required for stability. Strongly reduced tungsten skarns, characterized by garnet compositions with a low andradite content, possess highly variable almandine/spessartine ratios that are independent of andradite content (Fig. 9). These data and those of Shimazaki (1977) suggest that almandine and spessartine contents can vary considerably in garnet from skarns with less than 15 mole % andradite. The hyperbolic form of Figure 11 is thus explained by a co-operative substitution mechanism in subcalcic garnet. At moderately reduced oxidation states, a higher spessartine/almandine ratio is required as the andradite/grossular ratio rises, whereas at strongly reduced oxidation states, there is a limited amount of the andradite component that can be accommodated in a subcalcic garnet.

Subcalcic garnet and scheelite deposits

The relationship between low oxidation state and scheelite deposition in skarns has been suggested by several workers, *e.g.*, Einaudi (1977) and Shimazaki (1977). In zones of reduced calcium-ion activity, this low oxidation state is reflected by the presence of subcalcic garnet. In fact, the bulk of the world's scheelite resources are found in subcalcic-garnet-bearing skarns (Fig. 11). In addition, of the seven largest known scheelite-bearing skarns (> 6 million tons of ore), only one, the King Island deposit (Kwak & Tan 1981), does not contain subcalcic garnet.

Because of the retrograde and pressure-dependent solubility behavior of scheelite, tungsten skarns generally form at higher pressures and temperatures than those that characterize copper and base-metal skarns (Newberry & Einaudi 1981). Because the oxidation state during skarn formation is in part related to depth (Shimazaki 1980), deeper scheelite-bearing skarns should be characterized by more reduced mineral-assemblages, including subcalcic garnet. Except where hematitic host-rocks predominate or at depths transitional between scheelite and base metal skarns [*e.g.*, Lost Creek: Collins (1977), Tungsten Hills: Newberry (1980)], tungsten skarns were apparently buffered to oxidation states that would permit the formation of subcalcic garnet. Thus, although scheelite skarns lacking a subcalcic garnet do occur, they are less common and account for only a small fraction of known tungsten reserves.

Oxidized and reduced tungsten skarns also contrast in ore grades. Although grades are a function of tonnage, mining method, geographic location, extent of retrograde remobilization of tungsten, host rocks and other variables, the reduced (subcalcic garnet-bearing) skarns are characterized, in general, by higher tungsten grades (Fig. 12). This contrast can be found both between oxidized and reduced tungsten-skarn districts and also within districts that contain both types. In the Bishop district of California, for example, the oxidized andradite - quartz - epidote skarns of the Tungsten Hills area (Newberry 1980) contain grades of 0.2 to 0.5 % WO_3 (Bateman *et al.* 1950), whereas the moderately reduced subcalcic-garnet-bearing Pine Creek and Adamson mines are characterized by average skarn grades of 0.66 to 1.1% WO_3 (Bateman 1945). Similarly, in the Mount Morrison quadrangle, California, skarns adjacent to the Round Valley Peak granodiorite are in both highly graphitic and nongraphitic marbles. Reduced skarns, such as the Hardpoint and Pappas deposits, located in the highly graphitic Bloody Mountain Formation, are characterized by assemblages dominated by hedenbergitic pyroxene, possess subcalcic garnet compositions (Newberry 1980) and contain tungsten grades in excess of 1% WO_3 (Rinehart & Ross 1964). Oxidized skarns, such as the Scheelore mine, developed in the noncarbonaceous Mount Baldwin marble, are characterized by epidote - quartz - andraditic grandite ± pyrite assemblages, do not contain subcalcic garnet compositions (Morgan 1975) and have tungsten grades of 0.25 to 0.4% WO_3 (Rinehart & Ross 1964).

The relationship between skarn type and tungsten grade might be explained in terms of different P, T or $X(CO_2)$ of formation; however, differences in grade within skarns adjacent to the same pluton are suggestive of differences due to local state of oxidation. A proposed explanation is based on the observation that oxidized and reduced skarns are characterized by contrasting garnet/pyroxene ratios (Table 2). In particular, abundant pyroxene characterizes reduced skarns, and abundant garnet characterizes oxidized skarns (Einaudi *et al.* 1981). If a skarn-forming system deposits hedenbergitic pyroxene [owing in part to lower $f(O_2)$] that contains only 25 mole % CaO, then more calcium is available in the fluid to deposit scheelite than if the fluid deposits andraditic garnet, which contains 37.5 mole % CaO. In other words, in skarns formed from relatively pure marble, the higher the pyroxene/garnet ratio, the higher the average tungsten grade.

CONCLUSIONS

Garnet compositions intermediate between grandite and pyralspite are a characteristic feature of most tungsten-bearing skarns of western North America. Only those tungsten skarns formed from hematite-bearing host rocks or at relatively shallow depths do not possess subcalcic garnet. Garnet compositions, however, are far more variable and andradite-rich than indicated by previous studies. In fact, the subcalcic garnet of skarns can simultaneously contain more than 30 mole % andradite and 45 mole % almandine + spessartine component, and a garnet with as much as 65 mole % andradite may contain an appreciable subcalcic component. The occurrence of such garnet compositions requires (1) a moderately reduced environment of formation, approximately at or below the pyrrhotite - magnetite - pyrite buffer, and (2) a relatively low activity of the calcium ion in solution. Exceedingly variable almandine/andradite ratios occur in garnet compositions from a given skarn, in part owing to variable activity of the calcium ion and also to variable activity of the manganese ion. The presence of manganese is apparently required to stabilize the simultaneous presence of appreciable almandine and andradite components. In general, higher relative andradite contents in garnet require higher spessartine/almandine ratios for stability.

Tungsten-bearing skarns typically possess subcalcic garnet because they are characterized by

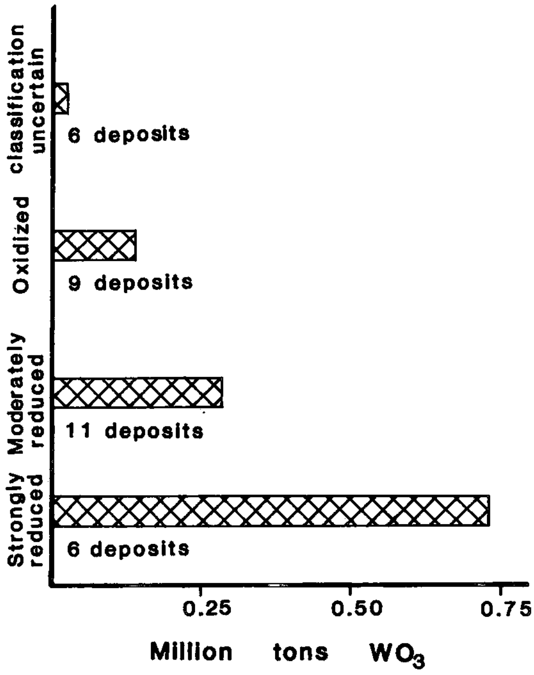

FIG. 11. Approximate known tonnages (production + reserves, expressed in tons contained WO_3) of the three classes of tungsten skarns discussed in this paper. Tonnage data from Einaudi *et al.* (1981). Note that the bulk of known WO_3 tonnage is from reduced (subcalcic-garnet-bearing) skarns.

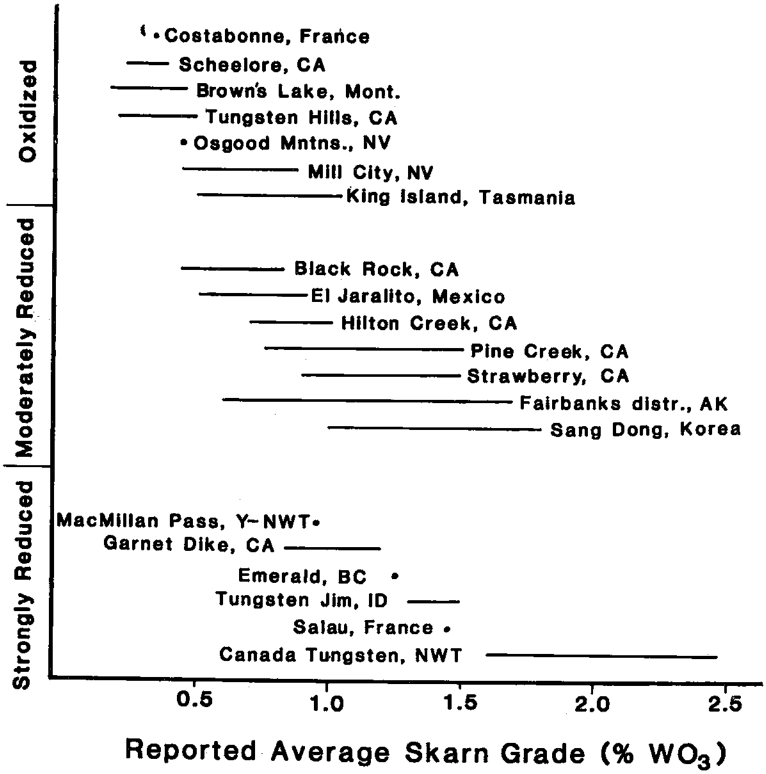

FIG. 12. Reported average tungsten grades from skarn ore *versus* skarn type. Note higher average grades associated with reduced rather than with oxidized skarns. Data from: Einaudi *et al.* (1981), Byers (1957), Bateman (1945), Rinehart & Ross (1964), Burchard (1977), Krauskopf (1953) and Peabody (1979).

moderate to low oxidation states, owing to wallrocks, an intrusion-buffered oxidation state and a depth of formation distinctly different from other skarn types. Because such skarns possess moderate to high pyroxene/garnet ratios, the presence of subcalcic garnet in a skarn is also linked to higher average tungsten grades. Thus, the presence of subcalcic garnet in skarns is not only of petrological and mineralogical interest, but also constitutes a potentially useful indicator of tungsten reserves.

ACKNOWLEDGEMENTS

The author is grateful to the Union Carbide Corp., Union Carbide Canada, Canada Tunsten, Teledyne Tungsten, and the Anaconda Company for permission to map and sample their deposits. Microprobe analyses were performed at Queen's University with the kind assistance of L.A. Dick and at University of California, Berkeley, with the assistance of M.L. Rivers. Some of the analyses at Berkeley were performed by D.C. Dobson. Discussions with Drs. M.T. Einaudi, L.A. Dick and L.D. Meinert assisted in the development of this research. Early versions of this manuscript were reviewed by J.M. Schmidt, D.C. Dobson, M.T. Einaudi and J. Trammell. The manuscript has also benefitted from extensive reviews by R.F. Martin, L.T. Trembath and two anonymous reviewers. Financial support from NSF grant EAR 78-19588 and from a grant by the Union Carbide Corporation is gratefully acknowledged.

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Received June 2, 1982, revised manuscript accepted February 3, 1983.