Abstract: Tungsten bearing endoskarns are developed in the Tenpo orebody of the Yaguki W-Cu-Fe mine, northeastern Japan, at the contact between the granodiorite and the slate by replacing both rocks. The endoskarn generally displays a zonal arrangement toward each original rock with successions of pyroxene skarn, garnet skarn enriched in andradite component, epidote skarn, garnet skarn enriched in grossular component and plagioclase-pyroxene skarn with prehnite veins. The mineral assemblage and mineral composition of each endoskarn is independent of its size and host rock composition, indicating that the same metasomatic process took place in the slate and the granodiorite. The coarse-grained primary hornblende and biotite in the granodiorite are altered into pyroxene, while plagioclases are into anorthite, epidote or garnet, in the endoskarn. The iron content in garnet, pyroxene and epidote decreases toward the host rock. Epidotes also decrease in their iron content with the progress of crystallization. The scheelite mineralization is divided into two stages. The earlier scheelite is characterized by high CaMoO$_4$ content (0.6-9 mol %) and occurs in association with pyroxenes, while the later scheelite contains low CaMoO$_4$ component (<0.3 mol %) and occurs in association with epidotes with low pistacite component (<20 mol %), prehnites and/or calcites. In spite of a local development of replacement textures between minerals, textural relations suggesting the prevalence of replacement reactions between skarn zones are not observed. The textural and geochemical data suggest that skarn zones were sequentially formed from the inner zone to the outer zone, in most cases by replacing host rocks directly rather than preexisting zones. It is inferred that the skarnization and tungsten mineralization at the Tenpo orebody was primarily related to the decrease in the concentration of Ca and Fe$^{3+}$ in the coexisting fluid.

1. Introduction

Skarn is classified on the basis of the host rock type into exoskarn and endoskarn, which are replacements of carbonates and aluminous rocks respectively. In general, the zonal arrangement is well developed in the endoskarn, and the mineralogy and mineral composition of the skarn display a systematic variation with ores and host rock lithology (EINAUDI et al., 1981). Analysis of the metasomatic process in the skarn zoning therefore provides insight into the genetical relationship between the skarnization and mineralization in a magmatic-hydrothermal framework. Replacement relations between skarn minerals are sometimes successfully traceable for endoskarns of granitic rock origin due to a well preservation of the primary texture in the granodiorite (e.g., NAKANO, 1978), while are difficult in most cases for endoskarns of the slate origin due to the equigranular texture and fine-grained minerals in the slate.

Previous studies have suggested that tungsten skarn deposits can be divided into two subclasses, reduced type and oxidized type (NEWBERRY, 1979) or W-Mo-Cu type and W-Sn-F type (KWAK and WHITE, 1982). Mineral assemblage and mineral composition of skarns is different between the two subclasses. Two stages of scheelites, scheelite with high Mo content in the earlier stage and low Mo content in the later stage, are a characteristic feature of the oxidized tungsten type. According to SHIMAZAKI (1980) and EINAUDI et al., (1981), the pyroxene-plagioclase skarn tends to occur in the reduced type, while the epidote-quartz skarn in the oxidized type. SHIMAZAKI (1969) described a wide distribution of epidote endoskarn of the slate origin from the No. 1 copper deposit in the Yaguki mine, while OGAWA and SHIDA (1975) reported a
presence of reduced plagioclase-pyroxene endoskarn from tungsten deposits in the same mine. The two types of scheelites and endoskarns occur in the slate and granodiorite replacements at the Tenpo orebody of the Yaguki mine. The purpose of this study is to describe the mode of occurrence of endoskarns and scheelites in the Tenpo orebody in order to elucidate the genetical relationship between the endoskarn formation and the scheelite mineralization.

2. Description of Geology and Skarn

The Yaguki mine is located at the southeast of the Abukuma massif, northeastern Japan. The surrounding geology of the mine is composed of slate, limestone and granitic intrusions. Skarns and ores widely distribute along the boundary between the limestone and the underlying slate of the Takakurayama formation of the Permian age (OGAWA et al., 1975; SHOJI et al., 1975; YANAGISAWA, 1967). The granodiorite batholith intrudes into the slate of the deposit. The K-Ar age of granitoids ranges from 88 to 100 Ma (KAWANO and UEDA, 1967).

The Tenpo orebody, a small tungsten orebody, is located at the southwest of the Yaguki mine. Endoskarns are developed along the boundary between the slate and the granodiorite, while limestones and exoskarns do not occur in this orebody. Fig. 1 shows the mode of occurrence of the endoskarns. Although the skarn occurrence at the Tenpo orebody is complex, the general succession of skarns observed toward each original rock is: (1) pyroxene skarn, (2) garnet skarn, (3) epidote skarn and (4) plagioclase-pyroxene skarn. Of these, the pyroxene skarn is locally distributed and occurs in contact with, or as a lense form in, the garnet skarn. Prehnite veinlets mainly occur in the plagioclase-pyroxene skarn. The individual skarn is variable in size from centimeter to meter. The vein skarn is conventionally termed for a single or zoned endoskarn which is developed near the host rock and with a vein form with below a few cm in width. It is difficult to illustrate in Fig. 1 due to its small size. Typical example of the vein skarn is shown in Fig. 2 (A3 and B2). In contrast, the massive skarn is termed for the skarn with mappable size. Because the massive skarn contains many veinlets and host rocks locally, the relation between the vein skarn and the massive skarn is not distinct but rather continuous.

2.1 Host rocks

The granodiorite is composed of quartz, plagioclase, K-feldspar, hornblende, biotite and sphene. Mafic minerals are in most cases altered into chlorite and calcite, and feldspars are into sericite in the vicinity of the deposits. Hornblendes around the orebody are often replaced by pyroxenes inwards from the rim (Fig. 3A). The slate is composed of quartz, plagioclase, chlorite and sericite. Biotites occur in the vicinity of the vein skarn.

2.2 Pyroxene skarn

The pyroxene skarn is dark green in color (Fig. 2A1) and distributes locally as a lense form in the garnet skarn. This skarn displays an equigranular Fig. 2 Photograph of the mode of occurrence of endoskarns. Abbreviations are as follows; Px: pyroxene skarn, G1: type-1 garnet skarn, G2: type-2 garnet skarn, Ep: epidote skarn, Pr: prehnite vein, Pl-Px: plagioclase-pyroxene skarn, S1: slate, Gr: granodiorite. A and B are endoskarns derived from the granodiorite and from the slate, respectively. A1: Relationship between pyroxene skarn and type-1 garnet skarn. A2: Zonal arrangement of the type-1 garnet skarn, epidote skarn and the plagioclase-pyroxene skarn. A3: Plagioclase-pyroxene skarn occurring in the epidote skarn. A4: Type-2 garnet skarn occurring as spots in the plagioclase-pyroxene skarn. A5: Prehnite veinlets in the plagioclase-pyroxene skarn. B1: Zonal arrangement of type-1 garnet skarn, epidote skarn, type-2 garnet skarn, plagioclase-pyroxene skarn and slate. B2: Vein skarn and its sketch. Prehnite veinlets mainly occur in the plagioclase-pyroxene skarn.
texture and is composed of prismatic pyroxene crystals with 0.5-1 mm in grain size. Pyroxenes often alter into amphiboles along the rim or the crack. Although there is a possibility that this skarn is limestone replacements due to its homogeneous composition, the gradual relationship of this skarn with the garnet skarn and other field observations suggest that this possibility is unlikely.

2.3 Garnet skarn

The garnet skarn is divided on the basis of the mode of occurrence into type-1 and type-2, which are spatially separated each other by the epidote skarn. The garnet skarn of the type-1 is pale to dark reddish brown in color (Fig. 2: A1, A2, B1 and B2). Its maximum width reaches to 5 m in the massive skarn and 70 cm in the vein skarn. Garnets of the type-1 are generally isotropic except some anisotropic garnets adjoining the epidote skarn and are often accompanied with small amounts of pyroxenes and interstitial quartz. Some dodecahedral garnets are replaced by epidotes in the vicinity of the epidote skarn (Fig. 3F). However, the microscopic observation shows that the whole texture of the epidote skarn was not formed by replacing the garnet skarn.

In contrast, the garnet skarn of the type-2 develops very locally between the plagioclase-pyroxene skarn and the epidote skarn (Fig. 2: B1) or as a spot in the plagioclase-pyroxene skarn (Fig. 2: A4), with the maximum width of several tens cm. The type-2 garnet skarn is orange with brownish tint in color and is composed of garnets with small amounts of epidote, calcite, pyroxene and quartz. This skarn tends to occur in sharp contact with the plagioclase-pyroxene skarn but to change gradually into the epidote skarn in some localities. Garnets occurring at the boundary of the plagioclase-pyroxene skarn have a tendency to include or replace the pyroxene (Fig. 3E).

2.4 Epidote skarn

The epidote skarn generally occurs in contact with the plagioclase-pyroxene skarn (Fig. 2: A2 and B2). It also develops between the type-1 garnet skarn and the plagioclase-pyroxene skarn (Fig. 2: A2 and B2) or the type-1 and type-2 garnet skarn (Fig. 2: B1 and B2). This skarn is composed of epidotes in association with pyroxene, amphibole, sphene, quartz, calcite and chlorite. Epidotes are generally present as an aggregate of anhedral to subhedral grains but tend to exhibit a euhedral form when are surrounded by calcites. Although the host rock of this skarn is not easily determined under the microscope, the replacement texture of primary hornblendes and biotites into pyroxenes are frequently observed in the epidote skarn of the granodiorite origin (Fig. 3D). Within the epidote skarn, the pyroxene tends to occur toward the type-1 garnet skarn, while the amphibole toward the plagioclase-pyroxene skarn. The sphene increases in the amounts toward the plagioclase-pyroxene skarn.

The birefringence of most epidotes are high, while epidotes with low birefringence locally distribute in intimate association with calcite veins (Fig. 3G) or interstitial calcites (NAKANO et al., 1989). It is notable in Fig. 3G that epidotes occurring along calcites display lower birefringences from white to pale blue than their surrounding epidotes with high birefringences from yellow to brown. The former epidotes are frequently observed in the prehnite vein.

2.5 Plagioclase-Pyroxene skarn

The plagioclase-pyroxene skarn is composed of plagioclase and pyroxene with small amounts of...
sphene. This skarn generally develops between the host rock and the epidote skarn (Fig. 2: A3 and B2) or the type-2 garnet skarn (Fig. 2: B1 and B2). The plagioclase-pyroxene skarn of the granodiorite origin is massive with 3 m in the maximum width and is in gradual contact with the granodiorite. Epidote or prehnite veins, of which width is generally narrow but locally reaches to a few cm, occur near the epidote skarn. The primary texture of the granodiorite is well preserved in this skarn. Pyroxenes occur as a replacement of primary coarse-grained hornblende (Fig. 3B) or biotite (Fig. 3C) in the granodiorite or as an aggregate of fine-grained crystals (mostly < 0.1 mm). Sphene occurs as an intimate association with pyroxenes.

On the other hand, the plagioclase-pyroxene skarn of the slate origin is a white-grey to grey in color and reaches to 1 m in the maximum width (Fig. 2: B1 and B2). Plagioclases and pyroxenes are generally fine-grained (below 0.1 mm), but sometimes are coarse-grained, reaching to 0.5 mm in the maximum. Both minerals are generally present as an aggregate. Pyroxene aggregates constitute a lense-form in, or alternate with, plagioclase aggregates (Fig. 3J).

2.6 Scheelite

Scheelites in the Tenpo orebody occur as veinlets or disseminations in the pyroxene skarn, the plagioclase-pyroxene skarn and the prehnite vein. Scheelites can be divided into two types from the fluorescent color (Fig. 3I). It is notable that scheelites occurring as disseminations in the plagioclase-pyroxene skarn and pyroxene skarn exhibit a yellow fluorescent color, while scheelites in the vein exhibit a blue one. Latter scheelites are commonly associated with calcites, prehnites and epidotes with low birefringences (Fig. 3H). However epidotes with high birefringence do not accompany any scheelites.

3. Chemical Composition of Skarns and Skarn Minerals

The bulk chemical compositions of the skarn and host rocks were determined by means of inductively coupled plasma-optical emission spectrometry (ICP-OES, with Jarrell-Ash model 750) and the mineral analyses were made by means of electron probe microanalysis (EPMA, JEOL JXA-8621). Both instruments are settled at the Chemical Analysis Center, University of Tsukuba. The analytical method for the ICP-OES is described in NAKANO et al. (1988). EPMA analyses were made for silicate minerals and for scheelites. Of eleven elements (Al, Ca, Cr, Fe, K, Mn, Mg, Na, Ni, Si and Ti) analysed quantitatively for the silicates, the Cr2O3 and NiO contents were all below 0.1 wt. %. The bulk composition of the rocks is given in Table 1. Representative EPMA data for pyroxene, garnet and feldspar are given in Tables 2, 3 and 4, respectively.

3.1 Bulk composition

Although the composition of major elements is highly variable even within a single skarn, its entire relationship throughout skarns and host rocks is best expressed by a ternary Ca-(Fe+Mn)-(Al+Mg) diagram (NAKANO, 1982). This is because (1) the mineral chemistry of skarn silicates are approximately expressed by binary Fe3+-Al (garnet, epidote and prehnite) and Fe2+-Mg (pyroxene and amphibole) solid solutions, (2) the Mn content in mafic skarn silicates tends to correlate sympathetically with Fe2+ content and (3) most skarn minerals differ in the Ca content one another. The ternary plot of the skarns and host rocks in the Tenpo orebody is given in Fig. 4. It is evident from this figure that (1) the two original rocks are plotted in the same region and (2) the Ca ratio decreases in the order of the garnet skarn, throughout epidote skarn, plagioclase skarn to host rocks, this order being qualitatively consistent with the spatial arrangement toward the host rocks.

Table 1 also shows that the concentration of alkali elements (Na, K) and Ba are lower in skarns than in host rocks, due to their large ionic radii for Ca skarn minerals and/or low concentration of alkali elements to Ca in the skarn-forming fluid. Epidote skarns contain high Sr contents than other skarns and host rocks, because Sr can substitute easily for Ca in the epidote. However, any systematic compositional difference between skarns and/or host rocks is not observed for other minor elements.

3.2 Pyroxene

Pyroxenes contain minor Na2O (0.1-0.8 wt.%) and Al2O3 (0.1-1.0 wt.%). However any systematic compositional relation is not observed
Table 1 Chemical composition of skarns and host rocks (ppm).

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Plagioclase- pyroxene skarn (granoctonite origin) | YG1076 | 118956 | 52 | 93579 | 29393 | 6147 | 19624 | 2572 | 18290 | 1113 | 14 | 286 | 6722 | 97 | 64 |

Table 2 Representative electron microprobe analyses of pyroxene.

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Table 3 Representative electron microprobe analyses of garnet.

| skarn | wt.% | Type1 | Massive | Si | Type1 | Massive | Si | Type1 | Massive | Si | Type1 | Massive | Si | Type1 | Massive | Si | Type1 | Massive | Si | Type1 | Massive | Si | Type1 | Massive | Si |
|-------|------|-------|---------|----|-------|---------|----|-------|---------|----|-------|---------|----|-------|---------|----|-------|---------|----|-------|---------|----|-------|---------|----|-------|---------|----|
| SiO₂  | 35.77 | 36.87 | 38.65 | 36.87 | 36.13 | 39.26 |
| Al₂O₃ | 0.27 | 6.35 | 13.81 | 20.63 | 7.60 | 22.23 |
| TiO₂  | 0.02 | 0.18 | 0.79 | 0.90 |
| FeO   | 29.94 | 23.25 | 12.14 | 2.79 | 21.60 | 53.87 |
| MnO   | 0.81 | 0.29 | 0.85 | 0.10 |
| MgO   | 0.12 | 0.11 | 0.12 |
| CaO   | 32.07 | 33.95 | 35.08 | 35.54 | 33.54 | 36.80 |
| Total | 98.92 | 100.73 | 100.85 | 100.64 | 98.92 | 98.83 |

Abbreviations are the same as Table 2.
Table 4 Representative electron microprobe analyses of feldspar.

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</tbody>
</table>

Number of ions on the basis of 8(O):

| Si     | 2.521 | 2.993 | 2.691 | 2.821 | 2.042 | 2.994 | 2.691 | 2.036 |
| Al     | 1.452 | 0.998 | 1.302 | 1.188 | 1.947 | 1.007 | 1.302 | 1.953 |
| Fe     | 0.009 | 0.004 | 0.007 | 0.001 | 0.007 | 0.003 |       |       |
| Ca     | 0.501 | 0.004 | 0.304 | 0.155 | 0.975 | 0.002 | 0.304 | 0.970 |
| Na     | 0.509 | 0.061 | 0.694 | 0.800 | 0.033 | 0.038 | 0.694 | 0.044 |
| K      | 0.011 | 0.943 | 0.005 | 0.040 | 0.148 | 0.005 | 0.002 |       |
| Total  | 5.003 | 5.003 | 5.003 | 5.004 | 4.997 | 4.990 | 5.003 | 5.008 |

Abbreviations are the same as Table 2.

![Fig. 4 Bulk Ca:Al:Mg:Fe+Mn ratio of host rocks and skarns.](image)

between the two oxides. The ternary Fe-Mn-Mg plot of the pyroxenes is illustrated in Fig. 5. The chemical composition of pyroxenes in the plagioclase-pyroxene skarn, epidote skarn and garnet skarn are plotted in the salite region (Di:51-76, Hd:22-45, Jo:2-4) and are not affected significantly by the host rock lithology, although pyroxenes in the plagioclase-pyroxene skarn is more variable in their Fe/Mg ratios than those in the epidote skarn and the garnet skarn. In contrast, pyroxenes of the pyroxene skarn have a distinct composition (Di:15-40, Hd:55-75, Jo:5-10) correspondent to the ferrosalite region. The chemical composition of pyroxenes which replaced limestones in the Yaguki mine are also illustrated in Fig. 5 for comparison. It is notable that pyroxenes of the exoskarn are more enriched in the hedenbergite and johannsenite component than those of the endoskarn in the Tenpo orebody. However, SUGAKI et al. (1989) reported the presence of ferrosalites in the Yaguki mine which formed by the secondary alteration of hedenbergiteprobably of limestone.

![Fig. 5 Ternary plot of clinopyroxene composition.](image)
Formation of endoskarn and scheelite at the Tempo orebody
The compositional variation of pyroxenes within a single zone is over the analytical precision (1 mol%). Although the core to rim compositional pattern of most pyroxene grains is not systematic, pyroxenes in the plagioclase-pyroxene skarn which replaced biotite and hornblende in the host granodiorite display an enrichment of Fe and Mn and a depletion of Mg around the rim (Fig. 6).

3.3 Garnet

The garnet contain small amounts of MnO (< 1 wt.% in most cases) and MgO (0.1-0.7 wt.%) (Table 2). Hence, the compositional feature of the garnets of the Tenpo orebody is approximately expressed by binary andradite (And)-grossular (Gr) join. It is evident from Fig. 7 that the type-1 garnet of the massive skarn decreases in the andradite content toward the outer epidote skarn, ranging from And_{100} in garnets which replaced the pyroxene skarn (YG1085), through And_{80-100} in garnets from the center of the garnet skarn (YG28M), to And_{25-50} in garnets at the contact with the epidote skarn (YG1110). The similar compositional tendency is also observed in type-2 garnets. As illustrated in Fig. 7, garnets in the center of the garnet skarn of the type-2 (YG1236) contain relatively high iron contents (And_{15-25}) compared to Al-rich garnets (And_{0-10}) at the contact with the plagioclase-pyroxene skarn (YG1119L).

The depletion of the iron content in the type-2 garnets is further observed in the vein skarn. Garnets of two vein skarn samples (YG-KO and YG1222) in Fig. 7 show that the andradite component is higher in the type-1 garnets than in the type-2 garnets.

3.4 Epidote

Epidotes generally occur as an aggregate of subhedral to anhedral crystals with high birefringence. Their pistacite component (Xps:Fe^{3+}/Fe^{2+}+Al) does not show any systematic core-rim compositional pattern within a single grain, while it tends to decrease toward the plagioclase-pyroxene skarn ranging from 0.28±0.04 down to 0.17±0.06 (NAKANO et al., 1989). However epidotes with Xps below 0.2 are rare in the epidote skarn. In contrast, zoned epidotes rarely occur where they are filled with calcites in their interstices or are associated with the calcite vein. The rim of the zoned epidote is characterized by low birefringence and low Xps below 0.2 (NAKANO et al., 1989). Fig. 8 shows the compositional map of Al
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**3. 5 Feldspar**

The composition of plagioclases in the granodiorite ranges from Ab$_{80}$An$_{20}$ to Ab$_{45}$An$_{55}$ (Fig. 9). In contrast, their replacements in the plagioclase-pyroxene skarn, coarse-grained plagioclases, are enriched in anorthite components of An$_{90-100}$ (YG1082 and YG1106). The well preservation of the primary granodiorite texture in the plagioclase-pyroxene skarn demonstrates that this enrichment of anorthite content is caused by the process similar to the cation exchange reaction between the anorthite and albite component. In contrast, fine-grained plagioclases which occur as interstices or veinlets in the coarse-grained anorthite have variable compositions ranging from Ab$_{15}$An$_{85}$ to Ab$_{85}$An$_{15}$ (Fig. 9). The textural evidence indicates that this enrichment of albite component is not ascribed to a compositional relict of primary plagioclase but is caused during the skarn-forming process in the latest stage. K-feldspar occasionally occur in association with these veinlets (Table 4). The similar compositional feature is also observed in plagioclases between the slate and its replacements (Fig. 9), although the textural relationship between the An-rich plagioclase and the Ab-rich one is not so evident in this case.

**3. 6 Scheelite**

Scheelites are not associated with garnets and Fe-rich epidotes (Xps>0.2) but coexist with pyroxenes, prehnites and Al-rich epidotes (Xps<0.2). According to SUGAKI et al. (1987), scheelites in the Yaguki mine can be divided into two stages; the earlier scheelite is characterized by a yellow fluorescent color and the relatively high CaMoO$_4$ content (>3 mole %), while the later scheelite is characterized by a blue fluorescent color and the relatively low CaMoO$_4$ content (<3 mole %). This is qualitatively applicable to scheelites in the Tenpo orebody (Fig. 3I). Fig. 10 shows the compositional mapping of W and Mo in scheelite. It is notable that Mo-rich scheelites (0.6-9 mol % in CaMoO$_4$) are overgrown by Mo-poor scheelites (<0.3 mol % in CaMoO$_4$) which are identical in composition to surrounding scheelites occurring as a veinlet. These compositional feature indicates
Fig. 9 Composition of plagioclases in the plagioclase-pyroxene skarn and the host rocks.

Fig. 10 X-ray intensity map of W and Mo in scheelites from the plagioclase-pyroxene skarn. Numbers in the column denotes the X-ray intensity (cps) of W and Mo. Note the rim of zoned scheelite is enriched in W and depleted in Mo and the rim composition has the same as scheelites in the veinlet.
that vein scheelites crystallized successively after the formation of core parts of disseminated scheelites. Presence of the two types scheelites are a diagnostic feature of tungsten skarn deposits in the oxidized tungsten type (EINAUDI et al., 1981).

4. Discussion

4.1 Skarn forming process

The same zonal arrangement, mineralogy and mineral composition are observed in the both endoskarns derived from the slate and the granodiorite in the Tenpo orebody, indicating that the same metasomatic process took place in the two aluminous host rocks. This is probably because the granodiorite and the slate have the similar composition with respect to major elements (Fig. 4). The replacement relation is well traced for endoskarns of the granodiorite origin, while it is very ambiguous for endoskarns of the slate origin. Hence, the textural and geochemical information from endoskarns hosted in the granodiorite may provide reliable constraints on the formation process of general endoskarns.

In the plagioclase-pyroxene skarn, primary mafic silicates and plagioclases in the granodiorite are converted into pyroxenes and anorthites, respectively. The difference of the alteration product indicates that the skarn mineral is highly controlled by the chemical composition of primary minerals to be replaced and/or the degree of their solubility into the skarn-forming fluid (NAKANO, 1978). The textural relationship of mafic silicates between Fig. 3A and 3B indicates that coarse-grained pyroxenes in the plagioclase-pyroxene skarn were formed by the direct replacement of primary mafic silicates with inward directions from the rim. The compositional map in Fig. 6 and the different mineral chemistry between the pyroxene and the amphibole further suggests that the replacement proceeded with the addition of Ca, Fe²⁺ and Mn²⁺ from the associated fluid into primary mafic silicates. In the case of plagioclase, the significant addition of Ca and Al from the skarn fluid and the concurrent extraction of Na and Si from the plagioclase may have converted the primary oligoclase-andesine plagioclase into the anorthite.

Garnet in the garnet skarn replace or include pyroxenes. This indicates that the garnet crystallized or continued to crystallize after the formation of pyroxene. The difference in the pyroxene composition between the garnet skarn and the pyroxene skarn (Fig. 5) suggests that the garnet skarn was not formed by the direct replacement of the pyroxene skarn, if pyroxenes did not alter their chemical composition during and after the replacement by garnets. On the other hand, pyroxenes which replaced the hornblende in the granodiorite are well observed in the garnet skarn (Fig. 3E), epidote skarn (Fig. 3D) and plagioclase-pyroxene skarn (Fig. 3B). These pyroxenes have a similar composition one another (Fig. 4), implying that the garnet skarn is a replacement of the plagioclase-pyroxene skarn. However, there is a possibility that the replacement of primary mafic silicates into salites occurred during or before the crystallization of garnet. In this case, the garnet skarn, and by extention the epidote skarn, can be formed even by the direct replacement of the primary granodiorite.

NAKANO et al. (1989) showed that the Xps of epidotes in the epidote skarn of the Tenpo orebody decreases toward the host rock and the zoned epidote decreases in the Xps toward the rim. They assumed that the high-Xps epidotes adjoining the garnet skarn formed in an earlier stage than low-Xps epidotes adjoining the plagioclase-pyroxene skarn. Low-Xps epidotes are observed in the calcite and prehnite veins which were formed in the latest stage. Similarly to epidotes, garnets also decrease in the Fe³⁺ content toward the host rock (Fig. 7). Considering that epidotes replace garnets at the boundary with the inward garnet skarn (Fig. 3F), these evidences may be explained by assuming that the garnet skarn and then the epidote skarn developed with replacing outward rocks, probably the primary granodiorite.

The geochemical data show that the similar metasomatic process may also have taken place in the slate. These textural and geochemical evidences are consistent with the zoned endoskarn which is developed in the diorite porphyry at the Shinyama deposit of the Kamaishi Cu-Fe mine (NAKANO, 1982). It is inferred from the comparison with the Shinyama endoskarns that a series of the Tenpo endoskarns may have progressively formed from the boundary between the granodiorite and the slate toward each host rock by the
direct replacement. It is also deduced from the geochemical data of the bulk composition and the mineral chemistry that the skarn formation of the Tenpo orebody was caused by the decrease of Ca and Fe$^{3+}$ concentration in the associated fluid.

4.2 Controlling factors responsible for the formation of endoskarns and scheelites

Shimazaki (1980) pointed out that the plagioclase-pyroxene skarn is stable under the relatively low fo$_2$ condition compared to the epidote skarn. He estimated the fo$_2$ boundary around the NNO buffer. However, this view is not straightforwardly applicable to the Tenpo orebody, since the two skarns at the Tenpo orebody were formed at the different stage and have a different chemical composition each other (Fig. 4). Uchida (1986) showed from the analysis of CaO-AL$_2$O$_3$-MgO-SiO$_2$-H$_2$O-CO$_2$ system that the plagioclase-pyroxene skarn is also stable at higher temperature than the epidote skarn. If each endoskarn at the Tenpo orebody was assumed to have successively formed in association with lowering in temperature, this may suggest that the plagioclase-pyroxene skarn was formed earlier than the epidote skarn. This possibility, although it can not be denied completely, appears unlikely.

Mo-poor scheelites at the Tenpo orebody occur in association with Al-rich epidotes and prehnites. According to Shoji (1977), the prehnite is unstable under the presence of small amounts of Fe$_2$O$_3$. Al-rich epidotes tend to be more stable under the low oxidation state than Fe$_2$O$_3$-rich epidotes (e.g., Keith et al., 1968; Liao, 1973). In contrast to the garnet and the epidote, some pyroxene grains are enriched in Fe$^{3+}$ and Mn around the rim (Fig. 6). The decrease of Fe$^{3+}$ in the garnet and the epidote and the increase of Fe$^{2+}$ in the pyroxene may be explained by the reduction of ferric ion into ferrous ion in the associated fluid. Hence, it appears that each endoskarn zone and two types scheelites developed successively with lowering in the oxidation state of the coexisting fluid.

5. Summary

Detailed examination on the occurrence and the geochemistry of zoned endoskarn, which is developed between the granodiorite and the slate at the Tenpo tungsten orebody in the Yaguki W-Cu-Fe mine, yields the following results.

(1) The general succession of endoskarns observed toward each original rock is the pyroxene skarn, type-1 garnet skarn enriched in andradite component, epidote skarn, type-2 garnet skarn enriched in grossular component and plagioclase-pyroxene skarn. Prehnite veins mainly develop in the plagioclase-pyroxene skarn. As the skarn occurrence is independent of the host rock lithology, the same metasomatic process may have taken place in the both host rocks.

(2) Endoskarns of the granodiorite origin is more suitable for the textural analysis of metasomatic replacements than those of the slate origin. The hornblende and biotite in the granodiorite is frequently replaced into the pyroxene in the garnet skarn, epidote skarn and plagioclase-pyroxene skarn. These pyroxenes are compositionally correspondent to salites but are different from ferrosalites of the pyroxene skarn and of the exoskarn in the Yaguki mine. Plagioclases are converted into anorthites in the plagioclase-pyroxene skarn, epidotes in the epidote skarn and garnets in the garnet skarn.

(3) The Fe$^{3+}$ content of the garnet and the epidote decrease systematically toward the host rock side. Epidotes also decrease in their Fe$^{3+}$ content with the progress of crystallization. This compositional feature is explained by assuming that the garnet skarn and then the epidote skarn was formed successively by replacing outward host rocks. In contrast to Fe$^{3+}$ containing minerals, the Fe$^{2+}$ content in the pyroxene of the plagioclase-pyroxene skarn increase toward the rim. Decrease of Fe$^{3+}$ and increase of Fe$^{2+}$ in skarn minerals may be attributed to the reduction of iron in the skarn-forming fluid.

(4) Scheelites do not coexist with garnets and Fe-rich epidotes (Xps>0.2). Mo-poor scheelites coexisting with prehnites, calcites and Al-rich epidotes formed in the later stage than Mo-rich scheelites disseminating in the pyroxene bearing skarn. The correspondence in the mineralogy and mineral chemistry of endoskarns with two types scheelites may suggest that the skarnization and mineralization at the Tenpo orebody were formed by lowering in the oxygen fugacity in addition to the decrease of the Ca and Fe$^{3+}$ concentration in the associated fluid.

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References


東北日本、八茎鉱山・天宝鉱体における
内成スカルンと灰重石の形成

高原弘幸・中野孝教

要旨：八茎タングステン・鉛・銅鉱山の天宝鉱体には、タ
ングステン鉱化作用を伴う内成スカルンが、花崗閃緑岩
とスレートの境界付近で同者を交代して発達している。さ
らに内成スカルンは、一般に源岩側に向けて、輝石スカ
ルン、アンドラライト成分に富むザクロ石スカルン、緑輝
石スカルン、クロシェロー成分に富むザクロ石スカルン、
斜長石-輝石スカルンと配列している。スカルンの鉱物組
み合せや鉱物組成は、スカルンの規模や源岩に拘らない
ことから、同じ交代作用が両源岩に関与した結果、一連の
スカルンが形成したことが伺える。内成スカルン内部で
は、花崗閃緑岩中の粗粒角閃石や粗粒黑雲母は輝石に、斜
長石は輝長石、緑輝石、ザクロ石に変化している。輝石、ザ
クロ石、緑輝石の鉱物性は源岩側に向けて減少している。
また緑輝石は後期のものほど鉱に乏しい。灰重石には二
つの鉱化時期が認められ、初期の灰重石は輝石と密接に
産し、高いCaMoO₄成分（0.6-9 モル%）で特徴づけられ
るのに対し、後期の灰重石はCaMoO₄成分が低く（0.3モル
%以下）、ビスタサイト成分の低い緑輝石、方解石、プドゥ
石と密接に産している。鉱物間での交代組織は局所的
に認められるものの、スカルン帯相互の間で交代作用が
生じたような組織は認められない。組織や化学組成から
推察すると、スカルン帯は両源岩の中心より外側の源岩
側に向かい、全体としては源岩を直接交代しながら形成
していったことが示唆される。スカルン化作用およびタ
ングステン鉱化作用は、関与した溶液のCu濃度や酸化状
態の減少する過程で生じたものであろう。