Skarns in the Kamioka mine

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Abstract

The Kamioka mine, Gifu prefecture, working the largest lead and zinc deposit in Japan, lies in the eastern corner of the Hida gneiss complex. The skarn minerals in this mining district are genetically divided into the following three groups.

Skarn A : Recrystallized skarn, formed by a regional metamorphism of impure limestone beds. The creation of skarn A is same in age to the formation of the Hida metamorphic complex.

Skarn B : Zoned skarn along the contact between limestone and Inishi syenitic rock, having a same origination to Shimonomoto granite. The formation of skarn B is closely related to the intrusion of Shimonomoto granite.

Skarn C : Pyrometasomatic skarn, formed by pyrometasomatic replacement of limestone probably after the deposition of the Mesozoic Tetori formation.

The ore deposits of the Kamioka mine are composed of the pyrometasomatic skarn (skarn C) called "Mokuji" and the hydrothermal deposits called "Shiroji". Skarn A and skarn B have no genetical relation to the ore deposits. But skarn A acts the valuable role for the stratigraphical classification of ore deposits and limestone beds.

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Introduction

During the years 1958 and 1959 the author gave special attention to the genetical classification of skarn minerals in the Kamioka mine. In this paper, occurrences and properties of the skarn minerals and their relationships to the surrounding geological features are described and discussed. Main part of this study was done when he was in Tokyo University. Recently he did some mineralogical reexamination in the Institute for Thermal Spring Research, Okayama University.

Location and Accessibility: Kamioka is situated in the northern part of Hida plateau, 25 km north northeast of Takayama city. It is linked to Takayama by a 33 km road and to Inotani by a 23 km mine track or road.

Acknowledgement: The author wishes to render grateful acknowledgement to Dr. T. Watanabe, Dr. T. Tatsumi and Dr. R. Sugiyama, whose criticisms and advices were of greatest service. He also expresses his thanks to the mining geologists of the Kamioka mine, especially to Mr. K. Shiobara, Mr. T. Sakuma and Mr. T. Sakai for their help during the field work.

Geology

This district is underlain by a thick sequence of folded and metamorphosed complex called Hida gneiss group. The complex has generally N to NNE strike and nearly vertical dip. But it is diposed in a NE direction near Tochibora and forms an anticlinorium whose pitching axis inclines to SW at 45°. Granitic rocks intrude along the southeastern margin of the complex. The southwestern part called Funatsu granite is characterized by pegmatitic texture and rose colored microcline. The northeastern one is known as Shimonomoto granite. Around Tochibora about 2 km in diameter, Inishi syenitic rock is exposed. A special feature on structure is the parallelism between the structure of Hida metamorphic complex and the boundary line of the complex to the granitic rocks. Augen gneiss is developed near the boundary. In northeastern part of this district, the metamorphic complex and the granitic rocks thrust over the Jurassic Tetori formation. The dip of thrust plane ranges from 30° SW to more than 60° SW. The older rocks are penetrated by many younger dikes of aplite, lamprophyre, quartz porphyry, porphyrite and andesite (Figure 1).

Hide metamorphic complex

The metamorphic complex around the mine is composed of biotite hornblende gneiss, hornblende gneiss, amphibolite, hornblende salite gneiss, crystalline limestone and quartzite. The commonest rock in the complex is biotite hornblende gneiss having well developed banding structure of mafic minerals. Several thin layers of amphibolite are interstratified with biotite hornblende gneiss. Amphibolite
Figure 1. Geological map

consists of predominantly green to greenish brown hornblende, which is associated with accessory minerals of andesine, ilmenite and apatite. Chemical analysis of the amphibolite collected from Maruyama 50 mL is given in the table below.

| Chemical composition of amphibolite, in weight percent |
|---------------------------------|-----------------|-----------------|
| SiO₂                            | 39.91           | CaO             | 10.92 |
| TiO₂                            | 2.21            | Na₂O            | 1.78  |
| Al₂O₃                           | 14.73           | K₂O             | 0.24  |
| Fe₂O₃                           | 4.57            | H₂O–             | 0.08  |
| FeO                             | 10.01           | H₂O+             | 3.06  |
| MnO                             | 0.18            | P₂O₅             | 0.06  |
| MgO                             | 12.13           | Total            | 99.88 |

Hornblende salite gneiss is narrowly distributed along limestone beds. Melanocratic band is mainly composed of salite ranging from Di₆₅ Hd₃₅ to Di₄₀ Hd₆₀ and biotite. Several beds of crystalline limestone are concordantly interstratified with these gneissose rocks. Limestone consists of even-grained colorless holocrystalline calcite averaging 5 mm in size. But towards northern part, near Mozumi the grain size of calcite gradually becomes smaller (0.1−0.5 mm).

Granitic rocks

Shimonomoto granite is mainly composed of quartz, orthoclase, oligoclase, biotite and hornblende. The medium grained homogeneous granite shows gneisso-

Figure 2. Chemical compositions of rocks

Skarns in the Kamioka mine

Inishi syenitic rock is coarse equigranular holocrystalline rock, composed of clinopyroxene, oligoclase, microcline and small amounts of sphene and apatite. The composition of clinopyroxene ranges from Di$_{30}$ Hd$_{70}$ to Di$_{30}$ Hd$_{70}$. Distribution of the syenitic rock is closely related with that of limestone. Boundary between Shimonomoto granite and the syenitic rock is assuredly gradual and both have same structural relation to gneiss complex. So, it is fully possible to think that they are different species having same origin and their difference was caused by the difference of contaminating rocks, that is — as a result of contamination Inishi syenitic rock was formed in limestone-area, while Shimonomoto granite was formed in gneiss-area. A-C-F diagram of figure 2 may support it. Their structural relations to the metamorphic complex are well observed in drifts, especially in the drifts for outside prospection of Tochibora deposit. A structural sequence of rocks is recognized from gneiss to granitic rock as shown in the next page.

Figure 3. Field relation of granitic rock to gneiss

1. The original structure of gneiss is kept in granitic rock. 2. The original structure of gneiss is reserved in the including relict. 3. The original rock is included at random as blocks in granitic rock in some cases. Arrangement of mineral having fluidal texture is recognized in metatect.
gneiss
arteritic rock or veined gneiss
agmatitic rock
nebulitic granite
homogeneous granite or syenitic rock

Width of “migmatite” zone is more than 10 m. Metatect of migmatite consists of Shimonomoto granite or Inishi syenitic rock. Paleozome is mainly composed of biotite hornblende gneiss, but in some cases biotite-enriched gneiss or limestone. The plutonic rocks possess both intrusive and replacemental characters. The field observations of them are shown in figure 3. Narrow contact metamorphic zone about 2 cm in width is developed along the contact between the plutonic rocks and the metamorphic complex. Characteristic minerals of the contact metamorphic zone are given in the following table.

<table>
<thead>
<tr>
<th>PLUTONIC ROCK</th>
<th>CHARACTERISTIC MINERAL OF CONTACT</th>
<th>ORIGINAL ROCK</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shimonomoto granite</td>
<td>biotite</td>
<td>hornblende gneiss</td>
</tr>
<tr>
<td>Shimonomoto granite</td>
<td>biotite</td>
<td>amphibolite</td>
</tr>
<tr>
<td>Inishi syenitic rock</td>
<td>biotite, ferrosalite, sphene</td>
<td>hornblende gneiss</td>
</tr>
<tr>
<td>Inishi syenitic rock</td>
<td>biotite, ferrosalite, sphene</td>
<td>amphibolite</td>
</tr>
<tr>
<td>Inishi syenitic rock</td>
<td>skarn B (described later)</td>
<td>limestone</td>
</tr>
</tbody>
</table>

Rose colored granite called Funatsu granite contacts with Shimonomoto granite through the zones of microcline-spotted granite and microcline-impregnated granite. Besides, augen gneiss or microcline-injected gneiss puts between the Hida gneiss complex and Funatsu granite. These intermediate zones are characterized by addition of microcline on account of the intrusion of Funatsu granite. So, the formation of Funatsu granite is successively later than that of Shimonomoto granite.

Genetical relation between the Hida metamorphic complex and these granitic rocks has not been clear still. Age of the metamorphic complex is said to be Precambrian. But some geologists believe it to be Permian according to the absolute age determination and the other geological evidences. If so, these granitic rocks may be serial products of a regional metamorphism.

Dike rocks

In this district, four kinds of dikes are found. Lamprophyre and aplite are the pre-ore dikes having close genetical relationship with granitic rocks. Several dikes of quartz porphyry are distributed in the high temperature zone of mineralization near Shikama valley. They are considered to be branches of ore bringer. Porphyrite may be a post-ore dike because it was never affected by mineralizing solution.
Ore deposit

Zinc, lead, silver, cadmium, bismuth and other metals are produced from the Kamioka mine. Sphalerite, galena, chalcopyrite, pyrite and magnetite are the chief metallic minerals.

Ore deposit called “Mokuji” mainly consists of hedenbergite which was formed by replacement of limestone. So, scale and form of the deposit are controlled by the original structure of limestone layers in the metamorphic complex. The pyrometasomatism was followed by a hydrothermal mineralization. The hydrothermal deposit named “Shiroji” develops outside the pyrometasomatic deposit. In detail, fissure system controls the distribution of “Shiroji”. Tochibora deposit is the most important one in the mine and lies just under Mt. Nijugoyama. It consists of several ore bodies which plunge to 40° SW. A large anticlinorium whose piching axis inclines to SW at 45° is recognized. Maruyama deposit about 2 km north of Tochibora is composed of a few monoclinic layers of pyrometasomatic hedenbergite skarn. It is rare in “Shiroji” in contrast to Tochibora deposit. Mozumi deposit is located 9 km north of Tochibora.

Classification of skarn

According to the author’s investigations, skarn minerals in the Kamioka mine and its neighbouring field are genetically divided into the following three groups.

Skarn A : Recrystallized skarn, zonally included in crystalline limestone.

Skarn B : Zoned skarn along the contact between limestone and Inishi syenitic rock.

Skarn C : Pyrometasomatic skarn which was formed by pyrometasomatic replacement of crystalline limestone.

Most ore deposits are composed of skarn C. Skarn A and skarn B have no genetical relation to the ore deposits. But skarn A is useful for stratigraphical classification of limestone and ore deposit.

Figure 4. Mode of occurrence of skarn A
(Futatsuya : sketch of outcrop)
Skarn A

Mode of occurrence and distribution

Crystalline limestone is divided into pure limestone, graphite bearing limestone and magnesian silicates bearing limestone. Associated minerals in limestone occur as bands which are completely parallel to gneissosity (Figure 4).

Mineral parageneses in skarn A

The following associated mineral assemblages are recognized.

(a) Pure limestone
   (1) calcite
(b) Graphite bearing limestone
   (2) graphite-calcite
(c) Magnesian silicates bearing limestone

Associated mineral assemblages in dolomitic limestone are shown in the SiO₂-MgO-Al₂O₃ diagram of figure 5-1. There are six kinds of mineral assemblage as follows:

(3) diopside-chondrodite-phlogopite-calcite-apatite
(4) diopside-phlogopite-pargasite-calcite-apatite
(5) diopside-pargasite-clinozoisite-calcite-apatite-sphene
(6) chondrodite-phlogopite-spinel-calcite-apatite
(7) diopside-wollastonite-calcite-clinozoisite-quartz
(8) chondrodite-spinel-calcite-dolomite

Assemblages of (3) and (4) are the commonest. Figure 5-2 shows the impure components of original limestone which is estimated from paragenetic relation.

Figure 5. Mineral assemblage in dolomitic limestone and estimated impure components

Calcite is usually associated. Apatite and sphene are rarely associated.
3,4. common. 5,6,7,8. rare.
Di: diopside  Ch: chondrodite  Pa: pargasite  Ph: phlogopite  Cz: clinozoisite
Sp: spinel  Wo: wollastonite  Do: dolomite
Besides, brucite, antigorite and prehnite are found in the same mode of occurrence. A part of brucite occurs primarily with phlogopite but most of it occurs as an alteration product of chondrodite. Antigorite is the commonest alteration product of chondrodite, spinel and diopside. As prehnite is usually associated with thulite or clinozoisite and occurs only in strongly altered zone, it is concluded to be a secondary mineral of alminous silicates.

The (a) and (b) are commoner than the (c) in the mining district. Any sulphide could not be found in skarn A.

Mineralogy

(a) Calcite

Crystalline limestone mainly consists of even-grained colorless holocry staline calcite averaging 5 mm in size. It is comparatively pure calcite and average composition of six calcites in limestone is as follows:

CaCO₃ 99.10  MnCO₃ 0.02  FeCO₃ 0.33
MgCO₃ 0.38  SrCO₃ 0.17

(b) Dolomite

In chondrodite bearing limestone in Maruyama, dolomite was found at first by X-ray method. In this specimen dolomite abuts on calcite whose properties are as follows: \( \omega = 1.568 \), \( a_{\text{hex}} = 4.985 \text{ Å} \), \( c_{\text{hex}} = 17.04 \text{ Å} \), \( (\text{Fe,Mn})\text{CO₃} = 0.2 \text{ mol %} \), \( \text{MgCO₃} \leq 0.8 \text{ mol %} \). According to X-ray investigation, dolomite and calcite are in ratio of 60 to 40 in maximum.

(c) Diopside

It occurs as an aggregate of colorless globular crystals being about 1 mm in diameter (Plate 1). Chemical composition and optical properties of mono-mineralic band of diopside in limestone of Maruyama are given in the table below.

<table>
<thead>
<tr>
<th>Chemical composition of diopside, in weight percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂ 52.51</td>
</tr>
<tr>
<td>TiO₂  tr</td>
</tr>
<tr>
<td>Al₂O₃ &lt;0.1</td>
</tr>
<tr>
<td>Fe₂O₃ 0.27</td>
</tr>
<tr>
<td>FeO 0.99</td>
</tr>
<tr>
<td>MnO 0.12</td>
</tr>
<tr>
<td>MgO 17.90</td>
</tr>
</tbody>
</table>

Calculated molecular percent of end members of pyroxene

| Diopside 94.2 | Johanssenite 0.4 |
| Hedenbergite 3.2 | Wollastonite 1.4 |
| Jadeite 0.8 |

Indeces of refraction : \( \alpha = 1.668 \), \( \beta = 1.674 \), \( \gamma = 1.687 \)

The X-ray powder-spacing data are given in the following table.
Takaharu Okuno

X-ray powder-spacing data for diopside

<table>
<thead>
<tr>
<th>d (A)</th>
<th></th>
<th>d (A)</th>
<th></th>
<th>d (A)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>3.35</td>
<td>1</td>
<td>2.217</td>
<td>w</td>
<td>1.626</td>
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<tr>
<td>3.24</td>
<td>10</td>
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<td>4</td>
<td>1.616</td>
<td>3</td>
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<tr>
<td>3.00</td>
<td>7</td>
<td>2.137</td>
<td>1</td>
<td>1.585</td>
<td>w</td>
</tr>
<tr>
<td>2.95</td>
<td>8</td>
<td>2.108</td>
<td>1</td>
<td>1.563</td>
<td>w</td>
</tr>
<tr>
<td>2.90</td>
<td>3</td>
<td>2.040</td>
<td>1</td>
<td>1.551</td>
<td>2</td>
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<tr>
<td>2.56</td>
<td>2</td>
<td>2.019</td>
<td>1</td>
<td>1.526</td>
<td>w</td>
</tr>
<tr>
<td>2.52</td>
<td>4</td>
<td>1.969</td>
<td>w</td>
<td>1.506</td>
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<tr>
<td>2.39</td>
<td>w</td>
<td>1.837</td>
<td>2</td>
<td>1.488</td>
<td>1</td>
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<tr>
<td>2.304</td>
<td>4</td>
<td>1.752</td>
<td>3</td>
<td>1.425</td>
<td>2</td>
</tr>
</tbody>
</table>

Refractive index $\beta$ of diopside in the same occurrence ranges from 1.674 to 1.680, indicating ratios from $\text{Di}_{10}\text{Hd}_{37}$ to $\text{Di}_{85}\text{Hd}_{11}$. According to X-ray fluorescent analysis, MnO content in these diopside is about 0.1% in weight.

(d) Chondrodite

It occurs as spherical yellowish grains, in which multiple twinning is never observed. So, it closely resembles to forsterite under the microscope. Any forsterite was never found during his investigation. Grain size ranges 0.5 mm to 5 mm. Refractive index $\beta$ is 1.605. The X-ray powder-spacing data for chondrodite collected from Inishi pass are given in the following table.

X-ray powder-spacing data for chondrodite

<table>
<thead>
<tr>
<th>d (A)</th>
<th></th>
<th>d (A)</th>
<th></th>
<th>d (A)</th>
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<tbody>
<tr>
<td>4.84</td>
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<td>3.025</td>
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<td>2.421</td>
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<tr>
<td>3.97</td>
<td>2</td>
<td>2.901</td>
<td>4</td>
<td>2.325</td>
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<tr>
<td>3.71</td>
<td>3</td>
<td>2.855</td>
<td>1</td>
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<tr>
<td>3.56</td>
<td>4</td>
<td>2.761</td>
<td>4</td>
<td>2.258</td>
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<tr>
<td>3.48</td>
<td>3</td>
<td>2.665</td>
<td>4</td>
<td>1.737</td>
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<td>2</td>
<td>2.620</td>
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<td>1.502</td>
<td>1</td>
</tr>
<tr>
<td>3.129</td>
<td>1</td>
<td>2.513</td>
<td>6</td>
<td>1.479</td>
<td>5</td>
</tr>
</tbody>
</table>

(e) Phlogopite

Phlogopite is present in euhedral brownish yellow crystals ranging 0.5 to 5 mm in length. Optical properties are as follows: $\beta=\gamma=1.566$, $2\gamma=\langle-\rangle$ small, $X=$colorless, $Y=$pale brown, $Z=$golden yellow. The X-ray powder-spacing data are given in the following table.

X-ray powder-spacing data for phlogopite

<table>
<thead>
<tr>
<th>d (A)</th>
<th></th>
<th>d (A)</th>
<th></th>
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<td>10.3</td>
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<tr>
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<td>2.622</td>
<td>1</td>
<td>1.684</td>
<td>6</td>
</tr>
<tr>
<td>5.07</td>
<td>10</td>
<td>2.529</td>
<td>10</td>
<td>1.537</td>
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<tr>
<td>3.74</td>
<td>2</td>
<td>2.238</td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.58</td>
<td>1</td>
<td>2.191</td>
<td>1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(f) Pargasite

It occurs as irregular shaped grains averaging 0.5～3
mm in length, associated with phlogopite or diopside. Optical properties are $2V=\pm 80^\circ$, $\beta=1.640$, $C/Z=14^\circ$ and colorless in thin section. But in some other crystal the following data are obtained. $2V=\pm 70^\circ$, $\beta=1.635$, $C/Z=21^\circ \sim 24^\circ$.

(g) **Spinel**  
It occurs as very small colorless grains on rare occasion. Sometimes it was replaced by fine grained fibrous antigorite. Though optical properties were not clearly determined, it is assumed to be magnesiospinel judging from the paragenetic minerals and alteration products.

(h) **Thulite or clinozoisite**  
The name of thulite is used as Mn bearing rose colored clinozoisite. The color ranges from rose to yellowish white. X-ray fluorescent analysis of most colored part shows the existence of iron (Fe$_2$O$_3$ 3\%\pm), manganese (MnO 1\%\pm) and strontium (1\%\pm). In X-ray properties, it corresponds with the thulite from Tataragi (A. Kato, 1958).

(i) **Wollastonite**  
Optical properties of wollastonite collected from Futatsuya are $\alpha=1.620$, $\beta=1.636$ and $Z/\Delta $elongation=2° $\sim$ 3° which indicate to be almost pure CaSiO$_3$.

(j) **Brucite**  
It is a secondary mineral of chondrodite and it occurs as fine grained anhedral crystals. On rare occasion, parallel intergrowth of phlogopite and brucite is observed.

(k) **Antigorite**  
It is an alteration product of chondrodite, spinel and diopside. It occurs as an aggregate of fine grained fibrous crystals whose optical properties are $\beta=1.56\pm$, birefringence=0.008, $2V=\pm$ small. These optical data indicate the serpentine being rich in antigorite molecule.

(1) **Prehnite**  
It may be a secondary mineral of alminous silicates. Clinozoisite or thulite is sometimes coated with small shapeless crystals of prehnite. Some prehnite shows fine lamellar twinning like one of microcline. $\beta=1.62\pm$, $\gamma-\alpha=0.020$ and colorless in thin section indicate a prehnite being rich in H$_2$Ca$_2$Al$_2$Si$_3$O$_{12}$ molecule.

(m) **Graphite**  
It is present in opaque tiny flakes of 1 $\sim$ 3 mm in length. In most of limestone in the mining district, graphite disseminates evenly throughout it. A zonal arrangement of graphite is obscurely observed in it.

(n) **Apatite and sphene**  
Apatite occurs as egg-shaped crystal of 0.1 $\sim$ 0.5 mm. Sphene occurs rarely as subhedral small grains.

**Skarn B**

**Mode of occurrence and distribution**

Zoned skarn occurs along the contact between limestone and Inishi syenitic rock. Width of the zone ranges from 0.5 cm to 5 cm. The syenitic rock has a narrow metamorphic zone along the contact with amphibolite and hornblende gneiss, too. Distribution of skarn B is restricted within the area distributing Inishi syenitic rock.
Zonal arrangement of skarn B

Skarn B is composed of wollastonite, grossularite, vesuvianite, ferrosalite, scapolite, sphene, apatite and pyrrhotite. Zonal sequences of main components of skarn B are given in the table below.

Zonal sequences of skarn B arranging from limestone to Inishi syenitic rock
(1) limestone  wollastonite  grossularite  ferrosalite  Inishi syenitic rock
(2) limestone  wollastonite  grossularite-vesuvianite  ferrosalite  Inishi syenitic rock

In the case of narrower zone ranging 1 mm to 5 mm in width, skarn B is commonly lacking in wollastonite and grossularite as shown below.
(3) limestone  ferrosalite  Inishi syenitic rock

Boundary between endomorphic and exomorphic skarn corresponds to the boundary of grossularite with wollastonite, judging from their microscopical texture and distribution of sphene. Chemical composition of the metamorphic zone inferred from their mode are given in the following table.

<table>
<thead>
<tr>
<th>Zone</th>
<th>Limestone</th>
<th>Wollastonite zone</th>
<th>Grossularite zone</th>
<th>Ferrosalite zone</th>
<th>Inishi syenitic rock</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>42</td>
<td>45</td>
<td>52</td>
<td>56</td>
<td>11</td>
</tr>
<tr>
<td>CaO</td>
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<tr>
<td>Al₂O₃</td>
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<tr>
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</tr>
<tr>
<td>Alkalis</td>
<td>0.5</td>
<td>3</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>TiO₂</td>
<td>calcite</td>
<td>wollastonite</td>
<td>grossularite</td>
<td>ferrosalite</td>
<td>microcline</td>
</tr>
<tr>
<td></td>
<td>graphite</td>
<td>calcite</td>
<td>ferrosalite</td>
<td>microcline</td>
<td>plagioclase</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>sphene</td>
<td>plagioclase</td>
<td>ferrosalite</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>sphene</td>
<td>apatite</td>
</tr>
</tbody>
</table>

SiO₂ content decreases gradually towards limestone side, while CaO content increases gradually. It is well explained that the zonal arrangement was formed by the reciprocal migration of SiO₂ and CaO at the contact. Mafic elements are generally more or less condensed along the front of the syenitic rock and they forms ferrosalite zone.

Mineralogy

(a) Wollastonite

The stretching direction of white fibrous crystal is perpendicular to the plane of contact. Optical properties of wollastonite collected from Tochibora -130 mL are α=1.622, β=1.640 and γ=1.640 and Z\ elongation=2°~3°, which
indicate a ratio of $\text{CaSiO}_3 : \text{FeSiO}_3 = 95 : 5$ in solid solution. The X-ray powder-spacing data are given in the following table.

<table>
<thead>
<tr>
<th>d (Å)</th>
<th>I</th>
<th>d (Å)</th>
<th>I</th>
<th>d (Å)</th>
<th>I</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.84</td>
<td>8</td>
<td>2.56</td>
<td>3</td>
<td>1.918</td>
<td>2</td>
</tr>
<tr>
<td>3.52</td>
<td>7</td>
<td>2.482</td>
<td>2</td>
<td>1.759</td>
<td>2</td>
</tr>
<tr>
<td>3.33</td>
<td>10</td>
<td>2.344</td>
<td>2</td>
<td>1.722</td>
<td>2</td>
</tr>
<tr>
<td>3.10</td>
<td>5</td>
<td>2.298</td>
<td>3</td>
<td>1.716</td>
<td>2</td>
</tr>
<tr>
<td>2.97</td>
<td>6</td>
<td>2.186</td>
<td>1</td>
<td>1.645</td>
<td>1</td>
</tr>
<tr>
<td>2.73</td>
<td>2</td>
<td>2.166</td>
<td>2</td>
<td>1.535</td>
<td>2</td>
</tr>
<tr>
<td>2.65</td>
<td>1</td>
<td>1.985</td>
<td>1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(b) *Grossularite* The garnet is externally rose or reddish brown, but colorless in thin section. It is present commonly as anhedral massive crystal having no optical anomaly. Refractive index (n) and lattice dimension ($a_0$) are given in the table below.

<table>
<thead>
<tr>
<th>locality</th>
<th>color</th>
<th>n</th>
<th>$a_0$ (Å)</th>
<th>estimated component from $a_0$</th>
<th>Gr : Ad*</th>
<th>Gr : Ad**</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tochibora ~130 mL</td>
<td>pale rose</td>
<td>1.734</td>
<td>11.86</td>
<td>95 : 5</td>
<td>100 : 0</td>
<td></td>
</tr>
<tr>
<td>Tochibora ~370 mL</td>
<td>pale rose</td>
<td>1.741</td>
<td>11.86</td>
<td>94 : 6</td>
<td>100 : 0</td>
<td></td>
</tr>
<tr>
<td>Tochibora ~130 mL</td>
<td>reddish brown</td>
<td>1.752</td>
<td>11.89</td>
<td>79 : 21</td>
<td>86 : 14</td>
<td></td>
</tr>
<tr>
<td>Maruyama 0 mL</td>
<td>chocolate</td>
<td>1.760</td>
<td>11.90</td>
<td>74 : 26</td>
<td>81 : 19</td>
<td></td>
</tr>
</tbody>
</table>

From X-ray fluorescent analysis, the maximum content of MnO is estimated to be 0.5 weight percent. Most of other rose colored garnets are estimated by X-ray method after Fleisher’s data to be $\text{Gr}_{0.92}\text{Ad}_0$.

(c) *Vesuvianite* It occurs as dark brown shapeless crystal whose optical properties are as follows: pale yellow in thin section, $\omega = \varepsilon = 1.72$, birefringence = 0.004, uniaxial negative. Sometimes it is intruded by veinlet of scapolite. The X-ray powder-spacing data for vesuvianite collected from Tochibora ~130 mL are given in the following table.

<table>
<thead>
<tr>
<th>d (Å)</th>
<th>I</th>
<th>d (Å)</th>
<th>I</th>
<th>d (Å)</th>
<th>I</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.72</td>
<td>1</td>
<td>3.48</td>
<td>3</td>
<td>3.20</td>
<td>3</td>
</tr>
<tr>
<td>4.02</td>
<td>2</td>
<td>3.34</td>
<td>2</td>
<td>3.046</td>
<td>5</td>
</tr>
<tr>
<td>3.85</td>
<td>2</td>
<td>3.24</td>
<td>3</td>
<td>2.947</td>
<td>6</td>
</tr>
</tbody>
</table>
Ferrosalite

The green pyroxene occurs as euhedral globular crystals, ranging in size from 2 mm to 10 mm. Diaglass parting is commonly observed but lamellar twinning cannot be found. Chemical composition and optical properties of ferrosalite collected from Inishi pass are given in the following table.

<table>
<thead>
<tr>
<th>Chemical composition of ferrosalite, in weight percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂ 48.57</td>
</tr>
<tr>
<td>CaO 22.51</td>
</tr>
<tr>
<td>TiO₂ 0.18</td>
</tr>
<tr>
<td>Na₂O 0.45</td>
</tr>
<tr>
<td>Al₂O₃ 2.56</td>
</tr>
<tr>
<td>K₂O 0.23</td>
</tr>
<tr>
<td>Fe₂O₃ tr</td>
</tr>
<tr>
<td>H₂O⁻ 0.00</td>
</tr>
<tr>
<td>FeO 19.99</td>
</tr>
<tr>
<td>H₂O⁺ 1.02</td>
</tr>
<tr>
<td>MnO 0.54</td>
</tr>
<tr>
<td>Fe₂O₃ 0.04</td>
</tr>
<tr>
<td>MgO 4.52</td>
</tr>
<tr>
<td>Total 100.61</td>
</tr>
</tbody>
</table>

Calculated molecular percent of end members of pyroxene

- Diopside 27.2
- Johannsenite 1.8
- Hedenbergite 66.5
- Wollastonite 1.0
- Jadeite 3.5

Index of refraction: α=1.713, β=1.720, γ=1.740

The X-ray powder-spacing data are given in the table below.

<table>
<thead>
<tr>
<th>X-ray powder-spacing data for ferrosalite</th>
</tr>
</thead>
<tbody>
<tr>
<td>d (Å)</td>
</tr>
<tr>
<td>4.51</td>
</tr>
<tr>
<td>3.35</td>
</tr>
<tr>
<td>3.27</td>
</tr>
<tr>
<td>3.00</td>
</tr>
<tr>
<td>2.19</td>
</tr>
<tr>
<td>2.585</td>
</tr>
</tbody>
</table>

Refractive index β measurement of the green pyroxenes ranges from 1.700 to 1.722, indicating a composition from Di₆₉ Hd₄₁ to Di₃₁ Hd₅₉.

Scapolite

It is not zoned skarn in strict meaning. It occurs as veinlet in vesuvianite, grossularite and Inishi syenitic rock near the contact. The X-ray powder-spacing data and optical properties of scapolite collected from Inishi pass are given in the following table. The data indicate that the scapolite is rich in meionite molecule.

<table>
<thead>
<tr>
<th>X-ray powder-spacing data for scapolite</th>
</tr>
</thead>
<tbody>
<tr>
<td>d (Å)</td>
</tr>
<tr>
<td>5.28</td>
</tr>
<tr>
<td>4.65</td>
</tr>
<tr>
<td>4.31</td>
</tr>
<tr>
<td>3.53</td>
</tr>
</tbody>
</table>
(f) Pyrrhotite  It was found in only one specimen of grossularite rock collected from Futatsuya. It occurs as a euhedral small grain with ferrosalite and grossularite.

(g) Apatite and sphene  Egg-shaped apatite and euhedral sphene occur in the metamorphic zone of the syenitic rock side of the contact.

Effects on skarn A of the skarnization forming skarn B

Relation of skarn B to skarn A is able to be observed in skarn A bearing limestone which is intruded by Inishi syenitic rock. A typical example is shown in figure 6. Inishi syenitic rock clearly cut the structure of skarn A and it had an effect on skarn A. Minerals of skarn A was assimilated by the syenitic rock and they disappeared. But only diopside remains as a relic mineral in the contact metamorphic zone or in the syenitic rock. The relic diopside occurs as a single crystal whose component changes gradually from core to outside of the crystal. The typical texture of it is shown in figure 7 and plate 2. It proves that Fe substitution for Mg osmotically progressed to inside of the relic diopside, as the frontal part of Inishi syenitic rock made an environment richer in iron.

Contact metamorphism of amphibolite and hornblende gneiss

Schematic relation of the contact between amphibolite and Inishi syenitic rock is shown in figure 8. Zonal sphene means the sphene including the core of ilmenite.

Figure 6. Field relation of skarn B to skarn A  
(Tochibora -130mL : sketch of wall)
Owing to assimilation by the syenitic rock, ilmenite altered gradually to sphene along the outside part of crystal. The same relation is observed in ferrosalite, in which a relic hornblende exists. Contact metamorphism of hornblende gneiss is almost similar. Width of the zone averages 2 cm.

Figure 7. Relic diopside in contact metamorphic zone

ferrosalite ($\beta = 1.716$) : green
diopside ($\beta = 1.676$) : colorless
plagioclase, sphene
microcline, apatite

Inishi syenitic rock
collected from Inishi pass

Figure 8. Contact between amphibolite and Inishi syenitic rock
(Maruyama 50 mL near cage)

1. Inishi syenitic rock. 2, 3. contact metamorphic zone. 4, 5. amphibolite.
Skarns in the Kamioka mine

Skarn C

Mode of occurrence and distribution

Zinc and lead bearing pyrometasomatic skarn, which was formed by replacement of crystalline limestone and a part of gneiss in the Hida metamorphic complex, is called skarn C in this paper. Except the hydrothermal "Shiroji" deposit, ore minerals are usually associated with silicates of skarn C, which is the largest in size in contrast with the other group of skarn. Skarn C is distributed specially in Tochibora, Maruyama, Mozumi, Inishi, Shimonomoto and so on. Scale and structure of these ore deposit consisting of skarn C are shown in figure 18. Ore minerals occur as anhedral crystals in the interstices, cavities and druses among hedenbergite mass.

Pyrometasomatism of limestone

As many kinds of limestone existed in strict meaning, the different kinds of product were formed by pyrometasomatic mineralization according to the difference of including impurities.

Pyrometasomatism of graphite bearing limestone

Graphite bearing limestone was changed to graphite bearing hedenbergite skarn. Graphite remains almost in situ but it is slightly moved or broken by the growth of hedenbergite crystal. Frontal margin of the hedenbergite skarn abuts sharply on the non-altered limestone.

Pyrometasomatism of diopside bearing limestone

Diopside bearing limestone was changed to diopside bearing hedenbergite skarn.

Figure 9. Relic diopside in hedenbergite crystal

hedenbergite : deep green
\[ \gamma = 48^\circ, \quad \beta = 1.732 \]
diopside : colorless
\[ \gamma = 38^\circ, \quad \beta = 1.674 \]
calcite

hedenbergite skarn collected from Maruyama - 10 mL
The diopside of skarn A is conserved during pyrometasomatism. Hedenbergite develops around the core of diopside as if a single crystal, which means the both of pyroxenes have the same optical orientation. The crystal of diopside core is mainly spherical, while enclosing hedenbergite is euhedral. Boundary of them is very sharp and never gradual (Figure 9 and plate 3).

**Pyrometasomatism of chondrodite bearing limestone**

Chondrodite bearing limestone was changed commonly to homogeneous hedenbergite skarn. Chondrodite disappeared at all owing to pyrometasomatism. But hedenbergite derived from this limestone has a tendency being richer in diopside molecule in contrast with hedenbergite from pure limestone. Along the front of pyrometasomatism, increasing of diopside molecule in hedenbergite is clearly observed. Namely, the boundary between hedenbergite skarn and chondrodite bearing limestone is gradual in appearance. A detailed description of the typical boundary is shown in figure 10. It is clearly proved from microscopical study that chondrodite or antigorite derived from chondrodite causes the gradual boundary.

**Pyrometasomatism of phlogopite-pargasite bearing limestone**

Phlogopite and pargasite were completely assimilated and never remain as relic minerals in pyrometasomatic skarn. Andradite bearing hedenbergite skarn occurs in skarnized part of phlogopite-pargasite bearing limestone of the several parts in the field. So it may be considered that andradite bearing hedenbergite originates in this kind of limestone. The following mode of occurrence of andradite may suggest it.

---

**Figure 10. Pyrometasomatism of chondrodite bearing limestone**

(Maruyama - I 0 mL)

<table>
<thead>
<tr>
<th>Color</th>
<th>Index</th>
<th>MnO</th>
</tr>
</thead>
<tbody>
<tr>
<td>dark bluish green, β = 1.727 (Hd 81%), wt%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>green, β = 1.712 (Hd 59%),</td>
<td></td>
<td>\checkmark</td>
</tr>
<tr>
<td>pale silky green, β = 1.698 (Hd 38%),</td>
<td></td>
<td>\checkmark</td>
</tr>
<tr>
<td>silky white, β = 1.687 (Hd 22%),</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Clinoxyroxene

Skarn C

Limestone

Tremolite zone

tremolite, which is derived from chondrodite

chondrodite bearing limestone
(1) Andradite seldom occurs in the skarn derived from pure or graphite bearing limestone, while it often occurs in a skarnized part of phlogopite-pargasite bearing limestone.

(2) It is sure from the following evidences that crystallization of andradite occurred after crystallization of hedenbergite. Andradite occurs with quartz or calcite in druse or cavity among hedenbergite crystals. On rare occasion tremolite associates with andradite in the cavity. The external form of andradite is controlled by the euhedral form of hedenbergite. In some cases many tiny euhedral hedenbergite are enclosed in a single crystal of andradite. Figure 11 shows the replacemental texture of andradite in hedenbergite. Under weak pyrometasomatism, chondrodite, phlogopite and pargasite decomposed to microlites of tremolitic amphibole and carbonate, which fill in the cavity of hedenbergite skarn. The form of the cavity is closely resemble to the external form of andradite (Figure 12). These facts may show that andradite derived from the microlites under

Figure 11. Replacement texture of andradite

![Image of replacement texture]

Figure 12. Mode of occurrence of andradite

1. andradite (g) and calcite (c) in druse of hedenbergite skarn (h).
2. microlites of carbonate and tremolitic amphibole (t) in druse of hedenbergite skarn (h).
stronger pyrometasomatism.

(3) Generally speaking, the garnet in hedenbergite skarn is almost pure andradite. But it has usually a little amount of alumina and the maximum determined content of Al₂O₃ is 8.43 % in weight. The alumina derived from decomposition of phlogopite and pargasite may contribute to form andradite.

**Pyrometasomatism of gneiss and Inishi syenitic rock**

Pyrometasomatic fluid attacked gneiss and granitic rock more or less. The width of metasomatosed gneiss is considerably narrower in contrast with that of limestone. The composing minerals of gneiss were almost replaced by epidote and quartz. The rock comprises 60～90 % in weight of euhedral grain of epidote, which should be called pistacite from its chemical property. Minute amount of apatite in gneiss is preserved but sphene altered to leucoxene. Besides, a reddened gneiss called “Yopparai gneiss” develops. The field relation of the “Yopparai gneiss” to the epidote-quartz rock is shown in figure 13. A dusty crystallite in feldspar makes the rock rose in appearance. The distribution of dusty feldspar is closely related to the minute veinlet of adularia.

**Pyrometasomatism of skarn B**

The field relation of pyrometasomatic skarn to skarn B is well observed in Maruyama. It is shown in figure 14. During pyrometasomatism, wollastonite

---

**Figure 13. Relation of epidote to Yopparai gneiss**

(Maruyama | +100 mL)

disappears but grossularite and ferrosalite remain *in situ* as relic minerals whose crystals are often sheared. Any chemical change of composition is not observed in the relic minerals.

**Figure 14.** Field relation of pyrometasomatic skarn to skarn B
(Maruyama 1–0 mL : sketch of roof)

1. hornblende gneiss. 2. epidote rock. 3. epidote-ferrosalite rock. 4. hedenbergite skarn. 5. andradite (\(a_0=12.05\), \(G_{r 7}\) Ad\(_{03}\), yellow). 6. grossularite (\(a_0=11.90\), \(G_{r 82}\) Ad\(_{18}\), chocolate). 7. quartz rock.

**Mineralogy**

(a) *Hedenbergite*  
It should be called manganese hedenbergite in strict meaning. The deep green clinopyroxene occurs as an aggregate of long prism ranging from 1 cm to 25 cm in length. Chemical composition and optical properties of manganese hedenbergite collected from Maruyama 1–0 mL are given in the following table.

<table>
<thead>
<tr>
<th>Chemical composition of manganese hedenbergite, in weight percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{SiO}_2)</td>
</tr>
<tr>
<td>(\text{TiO}_2)</td>
</tr>
<tr>
<td>(\text{Al}_2\text{O}_3)</td>
</tr>
<tr>
<td>(\text{Fe}_2\text{O}_3)</td>
</tr>
<tr>
<td>(\text{FeO})</td>
</tr>
<tr>
<td>(\text{MnO})</td>
</tr>
<tr>
<td>(\text{MgO})</td>
</tr>
</tbody>
</table>
Calculated molecular percent of end members of pyroxene

<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Diopside</td>
<td>5.5</td>
<td>Johannsenite</td>
<td>15.8</td>
</tr>
<tr>
<td>Hedenbergite</td>
<td>77.3</td>
<td>Wollastonite</td>
<td>0.2</td>
</tr>
<tr>
<td>Jadeite</td>
<td>1.2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Indeces of refraction: \( \alpha = 1.725 \) \( \beta = 1.732 \)

The X-ray powder-spacing data are given in the following table.

<table>
<thead>
<tr>
<th>( d (\text{Å}) )</th>
<th>( I )</th>
<th>( d (\text{Å}) )</th>
<th>( I )</th>
<th>( d (\text{Å}) )</th>
<th>( I )</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.77</td>
<td>4</td>
<td>2.557</td>
<td>4</td>
<td>1.637</td>
<td>4</td>
</tr>
<tr>
<td>4.25</td>
<td>1</td>
<td>2.238</td>
<td>1</td>
<td>1.585</td>
<td>1</td>
</tr>
<tr>
<td>3.35</td>
<td>4</td>
<td>2.191</td>
<td>4</td>
<td>1.578</td>
<td>1</td>
</tr>
<tr>
<td>3.28</td>
<td>6</td>
<td>2.151</td>
<td>3</td>
<td>1.510</td>
<td>1</td>
</tr>
<tr>
<td>3.01</td>
<td>10</td>
<td>2.122</td>
<td>2</td>
<td>1.449</td>
<td>3</td>
</tr>
<tr>
<td>2.91</td>
<td>1</td>
<td>2.014</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.592</td>
<td>3</td>
<td>1.778</td>
<td>3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The refractive index \( \beta \) of hedenbergite from Maruyama and Tochibora ranges from 1.720 to 1.733, which indicate the pyroxene ranging from \( \text{Di}_{10} \text{Hd}_{90} \) to \( \text{Di}_{50} \text{Hd}_{50} \) if \( \text{MnO} \) is negligible. But X-ray fluorescent analyses generally show the existence of a large quantity of \( \text{MnO} \).

(b) Andradite The subtransparent yellow garnet has usually zoned lamellar anisotropic character (Plate 4). Chemical composition of andradite collected from Maruyama \( \text{Vl-0mL} \) is given in the following table. The analysis

Chemical composition of andradite, in weight percent

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{SiO}_2 )</td>
<td>34.61</td>
</tr>
<tr>
<td>( \text{TiO}_2 )</td>
<td>0.08</td>
</tr>
<tr>
<td>( \text{Al}_2\text{O}_3 )</td>
<td>8.43</td>
</tr>
<tr>
<td>( \text{Fe}_2\text{O}_3 )</td>
<td>22.05</td>
</tr>
<tr>
<td>( \text{FeO} )</td>
<td>0.67</td>
</tr>
<tr>
<td>( \text{MnO} )</td>
<td>0.37</td>
</tr>
<tr>
<td>( \text{MgO} )</td>
<td>&lt;0.1</td>
</tr>
</tbody>
</table>

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CaO} )</td>
<td>33.25</td>
</tr>
<tr>
<td>( \text{Na}_2\text{O} )</td>
<td>0.13</td>
</tr>
<tr>
<td>( \text{K}_2\text{O} )</td>
<td>0.26</td>
</tr>
<tr>
<td>( \text{H}_2\text{O}^- )</td>
<td>0.05</td>
</tr>
<tr>
<td>( \text{H}_2\text{O}^+ )</td>
<td>0.23</td>
</tr>
<tr>
<td>( \text{P}_2\text{O}_5 )</td>
<td>0.06</td>
</tr>
<tr>
<td>Total</td>
<td>100.19</td>
</tr>
</tbody>
</table>

Calculated molecular percent of end members of garnet

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Almandine</td>
<td>1.5</td>
</tr>
<tr>
<td>Spessartite</td>
<td>0.9</td>
</tr>
<tr>
<td>Pyrope</td>
<td>0.0</td>
</tr>
</tbody>
</table>

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Grossularite</td>
<td>31.5</td>
</tr>
<tr>
<td>Andradite</td>
<td>66.1</td>
</tr>
</tbody>
</table>

\( a_0 = 12.03 \text{Å} \)

shows the existence of considerable amount of alumina. Analysed specimen is estimated by \( a_0 \) after Fleisher's data to be \( \text{Gr}_{19} \text{Ad}_{81} \). As the lattice dimension \( a_0 \),
of garnet remarkably increases owing to H₄ substitution for Si, it is quite possible to have a ingredient of hydrogarnet. The lattice dimension of andradite collected from the other places is shown in the following table. The composition of garnet in hedenbergite skarn ranges from Gr₁₉ Hd₃₁ to Gr₉ Hd₁₀₉, which is estimated by a₀.

### Lattice dimension of andradite

<table>
<thead>
<tr>
<th>locality</th>
<th>color</th>
<th>a₀ (Å)</th>
<th>estimated component from a₀</th>
<th>Gr : Ad*</th>
<th>Gr : Ad**</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maruyama VI</td>
<td>yellow ochre</td>
<td>12.06₂</td>
<td>0 : 100⁺</td>
<td>3 : 97</td>
<td></td>
</tr>
<tr>
<td>Maruyama I</td>
<td>yellowish brown</td>
<td>12.05₀</td>
<td>0 : 100⁺</td>
<td>9 : 91</td>
<td></td>
</tr>
<tr>
<td>Maruyama VI</td>
<td>yellow ochre</td>
<td>12.07₂</td>
<td>0 : 100⁺</td>
<td>0 : 100⁺</td>
<td></td>
</tr>
<tr>
<td>Jabara</td>
<td>yellowish brown</td>
<td>12.06₂</td>
<td>0 : 100⁺</td>
<td>3 : 97</td>
<td></td>
</tr>
<tr>
<td>Tochibora IV</td>
<td>yellowish brown</td>
<td>12.05₀</td>
<td>0 : 100⁺</td>
<td>9 : 91</td>
<td></td>
</tr>
<tr>
<td>Mozumi 0</td>
<td>yellow ochre</td>
<td>12.07₃</td>
<td>0 : 100⁺</td>
<td>0 : 100⁺</td>
<td></td>
</tr>
</tbody>
</table>

* based upon Skinner (1956).
** based upon Stockwell (1927) and Fleisher (1937).

(c) **Epidote**

Epidote is present as small yellowish green euhedral grain ranging from 0.1 mm to 1 mm in diameter and it is surrounded by anhedral quartz. Optical properties of the epidote are α = 1.727, birefringence = 0.040, which indicate a ratio of Ca₂Al₉(OH)Si₃O₁₂ : Ca₂Fe³⁺(OH)Si₃O₁₂ = 75 : 25. Chemical composition of epidote collected from Maruyama VI + 100 mL is given in the following table. Ca₂(Al₂.₈₁Fe₀.₆₃Fe₀.₈₈Mg₀.₀₂Mn₀.₀₃Ti₀.₀₂)(OH)Si₃O₁₂ is derived from the analysis after deducting impurity of quartz. It may well be called pistacite from its chemical composition.

<table>
<thead>
<tr>
<th></th>
<th>SiO₂</th>
<th>TiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>FeO</th>
<th>MnO</th>
<th>MgO</th>
<th>CaO</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>H₂O⁻</th>
<th>H₂O⁺</th>
<th>P₂O₅</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>42.97</td>
<td></td>
<td></td>
<td>19.62</td>
<td>9.55</td>
<td>1.06</td>
<td>0.43</td>
<td>42.97</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>42.97</td>
<td></td>
</tr>
<tr>
<td>TiO₂</td>
<td>1.42</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al₂O₃</td>
<td></td>
<td>19.62</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>9.55</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FeO</td>
<td>1.06</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MnO</td>
<td>0.43</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MgO</td>
<td>0.42</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(d) **Calcite**

It occurs as shapeless patches in the interstices of hedenbergite skarn. From the measurement of refractive index and lattice dimension,
it is deduced to be almost pure calcite. Average composition of four calcites in hedenbergite skarn is as follows:

<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCO₃</td>
<td>99.07</td>
<td>MnCO₃</td>
<td>0.40</td>
</tr>
<tr>
<td>MgCO₃</td>
<td>0.08</td>
<td>SrCO₃</td>
<td>0.08</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>FeCO₃</td>
</tr>
</tbody>
</table>

\[ \text{mol}\% \]

\[(e) \text{Quartz}\]

\[(f) \text{Lievrite}\]

Lievrite occurs as an euhedral crystal in the interstices of skarn with calcite and quartz. Mutual relation of lievrite to hedenbergite is similar to that of andradite.

\[(g) \text{Sphalerite}\]

It occurs as an anhedral crystal in the interstices of hedenbergite skarn with calcite, quartz and other ore minerals (Plate 5). Atomic ratio of Fe to Zn is 0.04 to 1 in sphalerite from Maruyama and 0.08 to 1 in sphalerite from Tochibora. FeS molecule in sphalerite of Tochibora averages 4.36 percent. Chalcopyrite spots of 10 \(\mu\) or less in diameter are commonly observed. These exsolutive spots of chalcopyrite are distributed at random or often arranged in a line. Round shaped grains of galena averaging 20 \(\mu\) in diameter are also found in sphalerite.

\[(h) \text{Galena}\]

\[(i) \text{Chalcopyrite}\]

Galena and chalcopyrite occur as fine grained exsolutive spots in sphalerite and as shapeless patches in the interstices of skarn.

\[(j) \text{Scheelite}\]

It occurs only in Jabara as anhedral crystals in the interstices of skarn.

\[(k) \text{Magnetite}\]

It occurs locally in Maruyama as thin lenticular layers in pyrometasomatosed gneiss.

**Hydrothermal deposit**

"Shiroji"

The pyrometasomatic mineralization followed a hydrothermal mineralization, which chloritized and replaced the mass of hedenbergite skarn and formed high grade ore deposit called "Shiroji". The hydrothermal deposit develops outside the pyrometasomatic deposit but the fissure system controls the distribution in detail. "Shiroji" is mainly composed of calcite, quartz and ore minerals.

**Mineralogy**

\[(a) \text{Calcite}\]

It is a main component of "Shiroji". Lattice dimension obviously decreases and refractive index \(\phi\) fairly increases in contrast with that of skarn A and skarn C. The comparison and the genetical consideration are described later. The average compositions of seven calcites in the typical replace-
mental Shiroji and three calcites from the calcite vein in the latest hydrothermal stage are as follows:

<table>
<thead>
<tr>
<th>Mineral</th>
<th>CaCO$_3$</th>
<th>MnCO$_3$</th>
<th>MgCO$_3$</th>
<th>SrCO$_3$</th>
<th>FeCO$_3$</th>
<th>mol %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shiroji calcite</td>
<td>96.74</td>
<td>1.73</td>
<td>0.19</td>
<td>0.15</td>
<td>1.19</td>
<td></td>
</tr>
<tr>
<td>Vein calcite</td>
<td>97.06</td>
<td>0.74</td>
<td>0.07</td>
<td>0.15</td>
<td>1.98</td>
<td></td>
</tr>
</tbody>
</table>

(b) **Quartz**  
It occurs commonly as euhedral crystals in the calcite rock.

(c) **Chlorite**

(d) **Sericite**

(e) **Hematite**  
Chlorite, sericite and hematite are hydrothermal alteration products of gneiss and granitic rock.

(f) **Sphalerite**  
Subhedral grains of sphalerite occur in the aggregate of calcite and quartz. Generally speaking, the exsolvative spots of chalcopyrite are poorer in contrast with that in the pyrometasomatic sphalerite. FeS molecule in the hydrothermal sphalerite averages 4.71 percent.

(g) **Galena**

(h) **Machildite**

(i) **Chalcopyrite**  
Chalcopyrite and quartz flood in the interstices of sphalerite, galena and hedenbergite. Veinlet of chalcopyrite intrudes along the crack of sphalerite.

(j) **Pyrite**  
A small amount of tiny euhedral pyrite occurs in the quartz-calcite rock.

**Comparison of minerals**

The properties of main minerals from the occurrences discussed above are compared each other in table 1.

**Pyroxene**

Three types of clinopyroxene from the mining district are plotted on MgO–FeO–MnO diagram (Figure 15). The pyroxene of skarn A occupies a domain of diopside in the diagram. As manganese and iron rarely existed in dolomitic limestone judged from the paragenetic minerals, almost pure diopside was formed by recrystallization. The pyroxene of skarn B occupies a domain of ferrosalite. FeO, MgO and MnO in Inishi syenitic rock are roughly 15 : 10 : 1 in molecule ratio. The composition of Inishi syenitic rock reflects on the composition of clinopyroxene along the contact. The pyroxene of skarn C is manganous hedenbergite. In the pyrometasomatic fluid, a large quantity of MnO is considered to have been
<table>
<thead>
<tr>
<th>GROUP</th>
<th>SKARN A</th>
<th>SKARN B</th>
<th>SKARN C</th>
<th>SHIROJI</th>
</tr>
</thead>
<tbody>
<tr>
<td>MINERAL</td>
<td>Calcite ((\text{Mg,Fe})\text{CO}_3&lt;0.1%)</td>
<td>Calcite ?</td>
<td>Calcite ((\text{Fe,Mn})\text{CO}_3&lt;0.1%)</td>
<td>Calcite ((\text{Fe,Mn})\text{CO}_3=3%)</td>
</tr>
<tr>
<td>Diopside</td>
<td>Ferrosalite</td>
<td>Mn-hedenbergite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dolomite</td>
<td>Grossularite</td>
<td>Andradite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Clinopyroxene</td>
<td>Gr\text{92Ad}</td>
<td>Gr\text{9Ad4}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chondrodite</td>
<td>Vesuvianite</td>
<td>Pistacite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Clinozoisite</td>
<td>Ca\text{2}(\text{Al}<em>{92.98}\text{Fe}</em>{2.7})\text{Si}<em>5\text{O}</em>{12}</td>
<td>Ca\text{2}(\text{Al}<em>{60-70}\text{Fe}</em>{20-30})\text{Si}<em>5\text{O}</em>{12}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wollastonite</td>
<td>Wollastouite</td>
<td>Quartz</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sphene</td>
<td>Sphene</td>
<td>Quartz</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Apatite</td>
<td>Apatite</td>
<td>Liévrite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Graphite</td>
<td>Scapolite rich in melonite</td>
<td>Tremolite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Brucite</td>
<td></td>
<td>Magnetite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Antigorite</td>
<td></td>
<td>Pyrite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Prehnite</td>
<td></td>
<td>Pyrite</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>GENESIS</th>
<th>Recrystallization of impure limestone</th>
<th>Contact metamorphism of Inishi syenitic rock</th>
<th>Pyrometamorphic replacement</th>
<th>Hydrothermal replacement</th>
</tr>
</thead>
<tbody>
<tr>
<td>OCCURRENCE</td>
<td>As bands in limestone parallel to gneissosity</td>
<td>As zoned skarn along the contact</td>
<td>“Mokuji” ore deposit</td>
<td>“Shiroji” ore deposit, controlled by fissure system</td>
</tr>
<tr>
<td>AGE OF FORMATION</td>
<td>Same in age to Hida gneiss complex</td>
<td>Same in age to Shimonomoto granite</td>
<td>After the deposition of Mesozoic Tetori formation</td>
<td></td>
</tr>
</tbody>
</table>
Skarns in the Kamioka mine

present in addition to FeO and SiO₂. The pyrometasomatic clinopyroxene from the zinc-lead mines in Mexico and New Mexico is usually rich in manganese. It may be a general rule that the clinopyroxene of zinc-lead bearing pyrometasomatic skarn is commonly manganoan hedenbergite or ferroan johannsenite.

Figure 15. Chemical composition of clinopyroxene

Garnet

Comparison of garnet between skarn B and skarn C is shown in the following table. Chemical and optical properties of them are clearly divided into the two groups. As the fluid forming skarn B originates in Inishi syenite rock in which much alumina exists, a large quantity of alumina entered into the garnet in addition to Fe₂O₃. But as pyrometasomatic fluid and limestone were lacking in alumina, the alumina-rich garnet was not formed in skarn C. Small amount of
alumina in the garnet is mainly derived from the crystallized impurities in limestone.

Calcite

Lattice dimension of calcite is given in figure 16. Chemical composition is given in figure 17. The analysed samples are mainly collected from Tochibora -130 mL and -300 mL. Both calcites of skarn A and skarn C are almost pure CaCO$_3$. But a small amount of iron and manganese exists in the calcite of skarn C, while

Figure 16. Lattice dimension of calcite

Figure 17. Chemical composition of calcite
manganese is absent in the calcite of skarn A. Calcite in Shiroji indicates the existence of considerable amount of MnCO₃ and FeCO₃ in solid solution of CaCO₃. It can be said that the variation on character of calcite occurred as a result of the effect of manganese and iron derived from decomposition of hedenbergite skarn in hydrothermal stage. Besides, it is noticeable that the pyrometasomatic sphalerite and calcite are poorer in Fe content than the hydrothermal sphalerite and calcite.

**Epidote**

Epidote occurs in skarn A and skarn C. From their chemical composition, they are clearly divided into the following two groups.

<table>
<thead>
<tr>
<th>SKARN A</th>
<th>SKARN C</th>
</tr>
</thead>
<tbody>
<tr>
<td>color</td>
<td>yellowish green</td>
</tr>
<tr>
<td>rose to white</td>
<td>yellowish green</td>
</tr>
<tr>
<td>refractive index</td>
<td>β = 1.721 ± 3</td>
</tr>
<tr>
<td>α = 1.725 ~ 1.728</td>
<td></td>
</tr>
<tr>
<td>birefringence</td>
<td>0.010</td>
</tr>
<tr>
<td>0.040</td>
<td></td>
</tr>
<tr>
<td>MnO (wt. %)</td>
<td>1.0 ±</td>
</tr>
<tr>
<td>0.5 ±</td>
<td></td>
</tr>
<tr>
<td>composition</td>
<td>Ca₂(Al₂₉₋₈₀Fe₇₋₈₀)₃(OH)Si₃O₁₂</td>
</tr>
<tr>
<td>Ca₂(Al₂₉₋₇₀Fe₇₋₈₀)₃(OH)Si₃O₁₂</td>
<td></td>
</tr>
<tr>
<td>species</td>
<td>clinozoisite</td>
</tr>
<tr>
<td>pistacite</td>
<td></td>
</tr>
</tbody>
</table>

**Genetical consideration**

Skarn A is the earliest product among various kinds of skarns in the field and it was affected by the later mineralization of skarn B and skarn C. Judging from occurrence and distribution, skarn A is thought to have the same origination to the Hida metamorphic complex. When limestone was recrystallized by a regional metamorphism, carbonaceous matter in limestone changed to graphite and dolomitic impurities created magnesian minerals. They are thought to be produced in situ by recrystallization without injection of any other mineralizing solution. Skarn B is obviously a contact metamorphic skarn related with the intrusion of Inishi syenitic rock. As Inishi syenitic rock cut the structure of skarn A bearing limestone, it is clear that the intrusion occurred in the post-age of the formation of skarn A. The creation of skarn C occurred after the formation of skarn B. The age of the pyrometasomaticism is surely later than that of the regional metamorphism and the intrusion of granitic rocks. It is inferred to be after the deposition of the Mesozoic Tetori formation from the following reasons.

It is well observed that pyrometasomatic mineralization attacked Shimonomoto granite, Inishi syenitic rock, and minerals of skarn A and of skarn B. A part of quartz porphyry dike in the post-Tetori formation was altered to sphalerite-chalcopyrite bearing epidote rock (Tochibora + 180 mL). The age of the pyrometasomatism is also inferred to be
1. Stage just after the Hida regional metamorphism.

<table>
<thead>
<tr>
<th>Mg silicates bg. limestone</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphite bg. limestone</td>
</tr>
<tr>
<td>Biotite hornblende gneiss</td>
</tr>
<tr>
<td>Amphibolite</td>
</tr>
</tbody>
</table>

2. Stage just after the intrusion of Shimonomoto granite (Permian).

<table>
<thead>
<tr>
<th>Shimonomoto granite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg. silicates bg. limestone</td>
</tr>
<tr>
<td>Graphite bg. limestone</td>
</tr>
<tr>
<td>Biotite hornblende gneiss</td>
</tr>
<tr>
<td>Amphibolite</td>
</tr>
</tbody>
</table>

3. Stage just after the pyrometamorphism (Post-Mesozoic age).

<table>
<thead>
<tr>
<th>Graphite bg. limestone</th>
<th>Graphite bg. hedenbergite skarn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chondrodite bg. limestone</td>
<td>+ Tremolite Salite ← Hedenbergite skarn</td>
</tr>
<tr>
<td>Phlogopite-pargasite bg. limestone</td>
<td>Andradite bg. hedenbergite skarn</td>
</tr>
<tr>
<td>Diopside bg. limestone</td>
<td>Diopside bg. hedenbergite skarn</td>
</tr>
<tr>
<td>Biotite hornblende gneiss</td>
<td>Yopparai gneiss</td>
</tr>
<tr>
<td>Inishi syenitic rock</td>
<td>Yopparai gneiss</td>
</tr>
</tbody>
</table>

Pyrometasomatic (ZnS PbS FeO MnO SiO₂) fluid

4. Stage just after the hydrothermal mineralization (Post-Mesozoic age).

<table>
<thead>
<tr>
<th>Gneiss</th>
<th>Chloritized gneiss</th>
</tr>
</thead>
<tbody>
<tr>
<td>Limestone</td>
<td></td>
</tr>
<tr>
<td>Hedenbergite skarn</td>
<td>Chloritized hedenbergite</td>
</tr>
<tr>
<td>Epidote rock</td>
<td>Chloritized gneiss</td>
</tr>
<tr>
<td>Inishi syenitic rock</td>
<td>Chloritized gneiss</td>
</tr>
</tbody>
</table>

Hydrothermal solution
after the Cretaceous from the viewpoint of a metallogenetic province, which includes the Nakatatsu mine, the Shimonomoto mine and the other zinc and lead mines located in the distributing area of the Mesozoic Tetori formation.

The mutual relations of these skarns are given in the schematic diagrams in page 92.

**Application to stratigraphical classification**

The crystalline limestone in the Hida metamorphic complex divided into pure limestone, graphite bearing limestone and magnesian silicates bearing limestone. As the features of each limestone are preserved during the pyrometasomatism, the stratigraphical classification of limestone beds is microscopically or megascopically possible even if they were completely replaced. The compiled map of figure 18 shows the stratigraphy in the mining district of the non-mineralized limestone and the ore deposit, which are classified by their mineralgical and chemical features.

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Figure 18  Compiled structural map of limestone and ore deposit in the Kamitsuka district
Plate 1  Diopside in crystalline limestone

(open nicol, $\times 25$)

Plate 2  Relic diopside in contact metamorphic zone

D : diopside  F : ferrosalite (open nicol, $\times 8$)
Plate 3 Relic diopside in hedenbergite crystal

Explanation of plate 3

D: diopside  H: hedenbergite  C: calcite  Q: quartz
Plate 4 Anisotropism of andradite

G : andradite  C : calcite (crossed nicols, ×25)

Plate 5 Sphalerite and calcite in hedenbergite skarn

S : sphalerite  C : calcite  H : hedenbergite (open nicol, ×25)