Petrological Characteristics of the Granitoids around the Yaguki Mine, Fukushima Prefecture, Japan.
—With Special Reference to the Relationships Between the Yaguki-Type Granodiorite and Ore Mineralization—

by

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(with 20 text-figures, 4 tables)

Abstract

Granodiorite bodies of the Yaguki-, the Ohbisagawa-, and the Yokokawa-types are distributed around the Yaguki contact metasomatic copper-iron and tungsten ore deposits. The tungsten mineralization might have occurred later than the copper-iron ore mineralization in the Yaguki ore deposit on the basis of field evidence. The Yaguki-type granodiorite (GD), lying beneath the ore bodies, is considered to be closely related to both of the ore mineralizations at the deposit. Based on the magnetic susceptibility and the mode of occurrences of Fe-Ti oxide minerals, the Ohbisagawa- and the Yokokawa-type granodiorites belong to the magnetite-series granitoids, while the Yaguki-type GD belongs to the ilmenite-series granitoids.

The upper intrusion surface of the Yaguki-type GD body dips gently to the northeast and shows local dome structures. The ore bodies are mostly distributed around these domes. Based on bulk chemical compositions, the distribution of alkali contents of the Yaguki-type GD is in accord with that of the ore bodies such as No.1, No.2, and the Nambu-Hinokiyama ore bodies. MnO content in ilmenite within the Yaguki-type GD body tends to increase toward the west as a whole and is not correlated to the D.I. of the host rocks. Although fluorine contents of apatite in the Yaguki-type GD do not greatly change with the increase in D.I., chlorine contents slightly increase with increasing D.I. in the early stage of magmatic differentiation (D.I. =64-68) and then decrease in the later stage (D.I. >68). Three-phase fluid inclusions, consisting of liquid, vapor, and halite, are observed in the Yaguki-type GD. On the basis of several assumptions, magma of the Yaguki-type GD might be initially unsaturated with water, but it became saturated with water during magma crystallization.

The differentiated magma of the Yaguki-type GD might be coexisted with an aqueous fluid containing chlorine and base metals. The aqueous fluids moved up to the sedimentary rocks above the granodiorite along the fissure zone. Mineralization occurred at the boundary between slate and limestone beds. Namely, not only the geologic structure but also the nature of magma might control the distribution of ore bodies in the Yaguki ore deposit.

Introduction

Various kinds of contact metasomatic ore deposits are known in the eastern part of the Abukuma belt associated with Cretaceous granitoids. The Yaguki ore

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deposit located at Iwaki City, Fukushima Prefecture, is one of representative contact metasomatic ore deposits in the province which produced copper, iron, and tungsten. Three granodiorites, the Yaguki-, the Ohbisagawa-, and the Yokokawa-types, are distributed around the Yaguki mine. It is considered that the Yaguki-type granodiorite (GD), found underneath the ore deposit, is closely related to the ore mineralizations of this deposit (Ogawa and Shida, 1975). Ogawa and Shida (1975) and Shoji et al., (1975) made clear that the distribution of ore bodies in the Yaguki ore deposit are controlled by local dome structures according to the Yaguki-type GD intrusion. In this ore deposit, ore mineralizations are divided into the copper-iron and the tungsten ore mineralizations (Ogawa and Shida, 1975; Muramatsu and Nambu, 1982). Predominant andradite and epidote (pistacite) in the skarn zone of this deposit suggest the formation conditions of higher oxygen fugacity than the NNO buffer line (Shimazaki, 1969, 1980). Shimazaki (1980) concluded that this deposit was related to the magnetite-series granitoids. Ogawa and Shida (1975) investigated tungsten ore mineralization at the Shimbu ore body, and presumed that tungsten ores closely associated with copper mineralization might be formed later than magnetite ores on the basis of field evidence. Muramatsu and Nambu (1982) inferred that tungsten ore mineralization might occur later than copper-iron ore mineralization on the basis of the data of fluid inclusions.

In this study, some characteristic petrological features of granitoids around the Yaguki mine were summarized. Special attention was devoted to making clear petrological characteristics of the Yaguki-type GD as a related igneous rock to the deposit. The relationship between granitic magmatism and ore mineralization at the Yaguki ore deposit is discussed from the viewpoint of the generation process of hydrothermal fluids from the granitic magma.

Geology and ore deposit at the Yaguki mine

Geologic Setting

The rocks around the Yaguki mine consist mainly of the Paleozoic formations and several igneous rocks, the Paleozoic formations being highly folded and/or faulted (Text-fig.1). The Paleozoic formations are divided into the Devonian Yaguki metamorphic rocks, the Carboniferous Yaguki Limestone Formation, and the Permian Matsuyamazawa Formation (Ministry of International Trade and Industry, 1987), and they have been intruded by the Yaguki-type GD. At the eastern end of this area, the Paleozoic formations are in fault contact with the Ohbisagawa-type GD, while the western end contacts with the Yokokawa-type GD by the Nekonaki fault (Yanagisawa, 1967) and/or by intrusive relation (Seki, 1962; Shimazaki, 1969).

The Yaguki metamorphic rocks consist mainly of black and green schists. Black schists are exposed in the northwestern part of this area, while green schists outcrop mostly in the northeastern part. The black schists seem to have originally been slates and sandstones, while the green schists were probably andesitic tuff or
Text-fig. 1 Geologic map and cross section around the Yaguki mine (modified from original map by the Shin-Yaguki mining Co., Ltd.). 1: slate (Matsuyamazawa F.); 2: limestone (Yaguki Limestone F.); 3: slate (Yaguki Limestone F.); 4: schist (Yaguki metamorphic rocks); 5: quartz-porphyry; 6: Yokokawa-type granodiorite; 7: Ohbisagawa-type granodiorite; 8: Yaguki-type granodiorite; 9: ultramafic rocks; 10: gabbro; 11: skarn; 12: tungsten ore body; 13: copper-iron ore body; 14: fault; No.1: No.1 ore body; No.2: No.2 ore body; No.3: No.3 ore body; No.4: No.4 ore body; AH: Asahiko ore body; SH: Nambu-Hinokiyyama ore body; AK: Akahage ore body.
lava (Seki, 1962). They belong to the glaucophane-schist to green-schist metamorphic facies (Seki, 1962).

The Yaguki Limestone Formation consists of slate and limestones. They have suffered low grade contact metamorphism due to the Yaguki-type GD intrusion and have been altered to biotite hornfels and crystalline limestones, respectively. Ore bodies of the Yaguki ore deposit are found in this formation. The Matsuyamazawa Formation is composed mainly of slate with thinly interbedded tuffaceous rocks and lenticular limestone beds.

Igneous rocks such as ultramafics, gabbroics, and granitoids also occur in this area. The ultramafic and gabbroic rocks were formed prior to the granodiorite activities (Ogawa and Shida, 1975). They intruded into the restricted area where metamorphic rocks are distributed. Large blocks of pyroxenite and dunite with partially serpentinized margins occur at the southern part of this area. Gabbro is found at the northern part.

Three types of granodiorite bodies, the Yaguki-, the Ohbisagawa-, and the Yokokawa-type GD, are distributed around this area. K-Ar ages indicate that these granodiorite bodies crystallized in Early to Middle Cretaceous time (Kawano and Ueda, 1967). These K-Ar ages are supported by the fact that the Ohbisagawa-type GD is unconformably covered with the Futaba Formation of Late Cretaceous age (Shimazaki, 1969). The Yaguki-type GD body occurs underneath the Yaguki Limestone Formation and crops out in the Nambu-Hinokiyama and the Akahage areas (Text-fig. 1).

Quartz-porphyry dikes are present in many places and intrude into the Yaguki-type GD, skarn, and copper-iron and tungsten ore bodies (Text-fig. 2). Therefore, quartz-porphyry intrusions probably occurred after the igneous activity of the Yaguki-type GD and the ore mineralization in the Yaguki ore deposit.

Ore Deposit of the Yaguki Mine

The Yaguki mine is composed of contact metasomatic copper-iron and tungsten ore deposits. The copper-iron ores are mainly composed of chalcopyrite, pyrrhotite and magnetite, and tungsten ores are composed of scheelite.

The skarn zone occurs along the boundary between limestone and slate beds in the Yaguki Limestone Formation (Text-fig. 1). Skarn is mainly composed of garnet, clinopyroxene, epidote and amphibole, and they show a distinct zonal distribution. The epidote-dominant skarns generally occur in the lower slate side, while the clinopyroxene-dominant skarns are found on the limestone side. The garnet-dominant skarns are interbedded between the epidote and clinopyroxene zones. The copper-iron and the tungsten ore bodies generally occur separately (Text-fig. 1). The copper-iron ore bodies are embedded in the skarn zone, especially in the garnet skarn, while tungsten ores occur mainly near the boundary between the skarn zone and the limestone, associated with clinopyroxene, epidote, quartz, sericite, calcite, and other minerals. The high grade magnetite ore is cut by scheelite-bearing quartz veinlets (Ogawa and Shida, 1975). At the 80mL W520 ore body
Text-fig. 2 Underground geological sketch at the 80 mL Shimbu W520 ore body. 1: Limestone with carbonaceous materials; 2: Quartz vein (Scheelite dominant part); 3: Quartz vein (Scheelite poor part); 4: Skarn; 5: Copper-iron sulfides ore; 6: Quartz-porphyry.

the copper-iron sulfides ore is also cut by scheelite-bearing quartz veins (Text-fig. 2). These facts suggest that the tungsten ore mineralization might have occurred later than the copper-iron ore mineralization. According to fluid inclusion studies by Muramatsu and Nambu (1982), filling temperatures for the copper-iron ore bodies are 270–360°C, while 200–300°C for the tungsten ore bodies. Muramatsu and Nambu (1982) also concluded that the tungsten ore mineralization might have occurred later than the copper-iron ore mineralization on the basis of the fluid inclusion data. However, small amounts of chalcopyrite is also associated with tungsten ore mineralization.

Mode of occurrence and petrography of the granitoids

The intrusive relationships among the Yaguki-, the Ohbisagawa-, and the Yokokawa-types GD are not clear from field occurrences around the mine. However, Kawano and Ueda (1963) reported that the K-Ar ages of these granodiorites are 110, 101, and 88 Ma, respectively.

Detailed mode of occurrence and petrography of individual granodiorites are
The Yaguki-type granodiorite

The Yaguki-type GD body is vastly distributed underneath the Yaguki Limestone Formation, and the exposures of the body are confined to a comparatively small area. The upper contact surface between the granodiorite body and the country rock slightly dips to the northeast, and the body shows dome structures at the No. 1 and No. 2 ore bodies (Text-fig. 3). Based on the modal proportions, this granodiorite can be classified as a fine- to medium-grained hornblende-biotite granodiorite to adamellite (Text-fig. 4), which has generally suffered hydrothermal alteration associated with the ore mineralization at the Yaguki ore deposit. At the No. 1 and the Tempo ore bodies scheelite occurs as disseminated ore in this granodiorite.

The major mineral constituents of the granodiorite are biotite, hornblende, plagioclase, quartz, and alkali feldspar. Volumetric ratios of biotite and hornblende are variable throughout the body.

Hornblende commonly occurs as euhedral to subhedral prismatic crystals with lengths of up to 2 mm, and includes poikilitically small amounts of ilmenite and apatite. The pleochroism of hornblende is $X'=\text{pale greenish yellow}$, $Y'=\text{yellowish brown}$, $Z'=\text{greenish yellow}$. Biotite occurs as anhedral to subhedral crystals up to 1.5 mm in length, or as aggregates of several grains associated with hornblende. Biotite occasionally occurs along the grain boundaries between euhedral plagioclase and hornblende crystals and shows kink-band textures. Therefore, it is believed that the crystallization of biotite occurred later than that of euhedral plagioclase and hornblende. The pleochroism of biotite is $X'=\text{pale yellow}$, $Y'=Z'=\text{dark brown}$. The biotite is partly altered to chlorite. Plagioclase generally occurs as euhedral to subhedral crystals up to 2 mm in length and occasionally shows zonal structures. Some of the plagioclase is sericitized, especially near the ore bodies. Quartz generally, less than 1 mm in size, occurs as anhedral crystals among plagioclase, hornblende, and biotite. Alkali feldspar also occurs as an anhedral crystals among plagioclase, hornblende, and biotite. It is often turbid in the interior. Perthite and microcline structures are not found.

Apatite, ilmenite, sphene, chalcopyrite, and pyrite are common accessories in the Yaguki-type GD. However, trace amounts of magnetite are locally found in the Nambu-Hinokiyama area. Chalcopyrite and pyrite generally occur in the boundaries among silicate minerals.

The Ohbisagawa-type granodiorite

The Ohbisagawa-type GD body is widely distributed in the eastern part of the area. It is composed of medium- to coarse-grained biotite-hornblende granodiorite (Text-fig. 4). The major mineral constituents are similar to the Yaguki-type GD, i.e. hornblende, biotite, plagioclase, quartz, and alkali feldspar.

Hornblende commonly occurs as euhedral to subhedral crystals up to 5 mm in
Text-fig. 3 Structural map of the Yaguki-type granodiorite body. Contour shows the height above the sea level (m) of the upper intrusion surface of the Yaguki-type granodiorite body. (Data of contour is modified from original map by the Shin-Yaguki mining Co., Ltd.)
length and contains small amounts of apatite, magnetite and ilmenite as inclusions. The pleochroism of hornblende is $X'=pale$ yellow, $Y'=Z'=green$. Biotite is present as subhedral to anhedral crystals up to 2.5 mm in size. The biotite is often slightly altered to chlorite and epidote along grain boundaries and cleavages. The pleochroism of the biotite is $X'=pale$ yellow, $Y'=Z'=brown$. Plagioclase generally occurs as euhedral to subhedral crystals up to 4 mm in length, and shows zonal structures. Quartz and alkali feldspar, up to 2 mm in size, occur as anhedral crystals among plagioclase and mafic minerals. The alkali feldspar shows a perthite structures. Apatite, zircon, sphene, and the Fe-Ti oxide minerals occur as accessories. The Fe-Ti oxide minerals, magnetite and ilmenite, are more abundant in
the Ohbisagawa-type GD than in the Yaguki- and the Yokokawa-types GD.

The Yokokawa-type granodiorite

The Yokokawa-type GD body is widely distributed in the western part of the area. It is composed of coarse-grained hornblende-biotite granodiorite to adamellite (Text-fig.4), and is characterized by the presence of quartz grains up to 1 cm in size. The major mineral constituents are biotite, hornblende, plagioclase, alkali feldspar, and quartz. Hornblende occurs as euhedral to subhedral crystals up to 1.5 mm in length. The pleochroism is X'=pale yellow, Y'=dark green, Z'=greenish brown. Biotite is present as subhedral to anhedral crystals and has a glomeroporphyritic texture. Plagioclase occurs as euhedral to subhedral crystals up to 4 mm in length, and shows zonal structures. Some of the plagioclase is strongly sericitized. Quartz is normally 1-7 mm in size, but some grains are up to 1 cm. Alkali feldspar occurs as anhedral to subhedral crystals with lengths of 1-4 mm, and shows both microperthite and microcline structures. Apatite, zircon, magnetite, and ilmenite occur as accessories. However, the amounts of magnetite and ilmenite in the Yokokawa-type GD are less than those in the Ohbisagawa-type GD.

Chemical characteristics

Granodiorites collected from the Yaguki mining area were chemically analyzed by wet methods and XRF analysis, and CIPW normative minerals were calculated on the basis of the chemical data (Table 1). The sampling sites of the Yaguki-type GD are shown in Text-fig.5. Most of samples of the Yaguki-type GD were collected from near the upper intrusion surface (Text-fig.5).

The major oxides were plotted to determine their variation in percentage against SiO₂ content (Text-fig.6). The SiO₂ content ranges from 64 to 74 wt. % (D.I.=65-87) in the Yaguki-type GD, from 66 to 70 wt. % (D. I.=68-77) in the Ohbisagawa-type GD, and from 69 to 70 wt. % (D. I.=75-81) in the Yokokawa-type GD. In comparison with average Japanese granitoids (Aramaki et al., 1972) the Yaguki-type GD is characterized by relatively higher contents of CaO and lower TiO₂ and total Fe. The Ohbisagawa-type GD shows higher Al₂O₃, CaO, and Na₂O contents and lower total Fe and MgO contents. The Yokokawa-type GD shows higher Al₂O₃ and K₂O contents and lower TiO₂, total Fe, and MgO contents. These granodiorites can be distinguished by K₂O/Na₂O ratios of their chemical compositions. Namely, the Yokokawa-type GD has high K₂O/Na₂O ratios, while the Ohbisagawa-type GD has low K₂O/Na₂O ratios and the Yaguki-type GD has an intermediate K₂O/Na₂O ratios (Text-fig.7).

On the AFM diagram (Text-fig.8), the three types of granodiorites have the same trend which resembles that of calc-alkaline rocks, although plots of the Yaguki-type GD are slightly shifted to the MgO dominant field in comparison with other two granodiorites.

The normative compositions of the three types of granodiorites have been plot-
Table 1 Representative chemical compositions and magnetic susceptibilities of the granitoids around the Yaguki mine.

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Q | 21.03 | 22.50 | 24.84 | 23.24 | 28.19 | 32.86 | 23.83 | 25.58 | 25.41 | 24.10 | 20.93 |

or | 17.31 | 17.43 | 17.13 | 19.55 | 15.54 | 27.06 | 14.36 | 16.66 | 20.85 | 27.18 | 19.67 |

ab | 28.42 | 27.32 | 29.44 | 33.07 | 30.79 | 27.32 | 29.52 | 35.10 | 29.10 | 29.77 | 27.83 |

an | 17.15 | 18.97 | 17.83 | 14.78 | 18.74 | 7.89 | 19.10 | 12.64 | 14.17 | 11.26 | 17.70 |

C | 3.68 | 0.08 | 0.14 | | | | | 0.73 | 1.17 | 1.17 | 1.48 | 1.39 |

Dl | 4.38 | 5.13 | 4.06 | 3.24 | 2.49 | 1.40 | 3.31 | 2.79 | 2.64 | 1.94 | 2.19 |

H₂O | 3.57 | 4.61 | 3.28 | 1.91 | 1.12 | 0.56 | 6.74 | 4.54 | 4.52 | 3.81 | 7.62 |

Mt | 1.46 | 1.42 | 1.39 | 1.73 | 0.83 | 1.04 | | | | | |

Il | 0.91 | 0.95 | 0.74 | 0.57 | 0.55 | 0.23 | 0.93 | 0.63 | 0.63 | 0.47 | 0.74 |

Ap | 0.31 | 0.19 | 0.12 | 0.21 | 0.19 | 0.19 | 0.21 | 0.17 | 0.17 | 0.14 | 0.17 |

D. L. | 66.76 | 67.25 | 71.41 | 75.87 | 74.52 | 87.24 | 67.71 | 77.34 | 75.36 | 81.05 | 68.43 |

χ** | 35.70 | 46.22 | 79.53 | 79.22 | 50.88 | 58.03 | 252.95 | 555.96 | 200.64 | 107.95 | 165.67 |

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# Chemical compositions were determined by wet method (Analyist: T. Hirano).
## Chemical compositions were determined by XRF analysis.
* Total Fe as FeO.
** Magnetic susceptibility (×10⁻⁶ emu/g).
1-6: Yaguki-type granodiorite
7-8: Ohbisagawa-type granodiorite
9-10: Yokokawa-type granodiorite
11: Quartz-porphyry
Text-fig. 5 Sampling sites of the Yaguki-type granodiorite. Numbers with symbols show the height of sampling sites above the sea level (m). Contour lines are the same as for Text-fig. 3.
ted on the Qtz-Ab-Or diagram (Text-fig. 9). Water pressure of the granodiorite having a high differentiation index (D. I. = 87) in the Yaguki-type GD is estimated to be about 1.5 kb by the experimental data (Tuttle and Bowen, 1958; Luth et al., 1964) in the system Qtz-Ab-Or-An-H$_2$O.

Text-fig. 10 shows the distribution of alkali contents ((Na$_2$O+K$_2$O)/(Na$_2$O+K$_2$O+MgO+FeO)×100(%) ) within the Yaguki-type GD body. This variation pattern has a WNW-ESE trend, and the area from the No. 1 ore body to the Nambu-Hinokiyama area shows relatively higher values of alkali content (more than 60%). The area showing high alkali content may be the area where magmatic

Text-fig. 6 Oxides-SiO$_2$ variation diagrams for the granitoids around the Yaguki mine. Open circles: Yaguki-type GD with D. I. of less than 80; Solid circle: Yaguki-type GD with D. I. of more than 80; Open squares: Ohbisagawa-type GD; Open triangles: Yokokawa-type GD; Crosses: Quartz-porphyry. Lines show the average compositions of granitoids in Japan (Aramaki et al., 1972).
Text-fig. 7 $K_2O/Na_2O-SiO_2$ variation diagram for the granodiorites around the Yaguki mine. Symbols are the same as for Text-fig. 6.

Text-fig. 8 Differentiation trend of the granitoids around the Yaguki mine plotted on the $(Na_2O+K_2O)-Total\;Fe\; (as\; FeO^*) - MgO$ (AFM) diagram. Curve shows the trend of the calc-alkaline rock series. Symbols are the same as for Text-fig. 6.

Text-fig. 9 Normative compositions of granitoids around the Yaguki mine plotted on the normative quartz-albite-orthoclase diagram. Symbols are the same as for Text-fig. 6. The quartz-feldspar boundary in the granite system, $SiO_2 - NaAlSi_3O_8 - KAlSi_3O_8 - H_2O$, is shown for 0.5, 1, 2, 3, 5, and 10 kilobars water pressure (Tuttle and Bowen, 1958; Luth et al., 1964).
differentiation progressed. This pattern is in harmony with the internal foliation structure of the granodiorite body (Text-fig. 3).

**Text-fig. 10** Distribution map of $(\text{Na}_2\text{O} + \text{K}_2\text{O})/(\text{Na}_2\text{O} + \text{K}_2\text{O} + \text{total FeO} + \text{MgO}) \times 100(\%)$ within the Yaguki-type granodiorite body. Open circles: data from Ministry of International Trade and Industry (1987); Solid circles: this study.
Fe-Ti oxide minerals

Mode of occurrence

Usually, small amounts of Fe–Ti oxide minerals are identified as accessory minerals in the granodiorites around the mine. The granodiorites can be divided into two types based on the mode of occurrence of Fe–Ti oxide minerals. The Ohbisagawa- and the Yokokawa-types GD contain both magnetite and ilmenite, while the Yaguki-type GD is characterized by the absence or the scarcity of magnetite. Ishihara (1979) mentioned that magnetite-bearing granitoids have higher values of magnetic susceptibility ($\chi > 100 \times 10^{-6}$ emu/g) than magnetite-free ones. The magnetic susceptibility data of the granitoids around the area are in accord with the mode of occurrences of Fe–Ti oxide minerals (the Yaguki-type GD: $\chi < 80$; the Ohbisagawa-type GD: $\chi = 250–550$; the Yokokawa-type GD: $\chi = 100–200 \times 10^{-6}$ emu/g; see Text-fig. 11). Magnetite and ilmenite are generally observed as granular grains within mafic minerals such as biotite and hornblende.

The Yaguki-type GD usually contains a maximum of 0.7 vol. % ilmenite (magnetite-free type). Both magnetite and ilmenite are, however, observed even in the Yaguki-type GD at the Nambu-Hinokiayama area (magnetite-bearing type). A lower magnetic susceptibility is observed in the central and eastern parts of the body, while a higher magnetic susceptibility is observed in the western part (Text-fig. 12). This distribution pattern is in harmony with the mode of occurrence of magnetite. Ilmenite occurs as subhedral to anhedral crystals of 20 to 250 microns in size. Magnetite is present as euhedral to anhedral crystals up to 600 microns in size. Some of the magnetite grains have ilmenite lamellae of about 10 microns in width. Fe–Ti oxide minerals generally do not coexist with sulfide minerals such as pyrrhotite, pyrite, and chalcopyrite.

The Ohbisagawa- and the Yokokawa-types GD usually contain both magnetite and ilmenite in them. Some of the magnetite grains show the intergrowth of thin ilmenite lamellae. The Ohbisagawa-type GD has higher amounts of Fe–Ti oxide minerals in volume than the Yaguki- and the Yokokawa-type GD.

Chemical compositions of Fe–Ti oxide minerals

![Text-fig. 11 Histogram of the magnetic susceptibility ($\times 10^{-6}$ emu/g) of granodiorites around the Yaguki mine.](image-url)
Chemical compositions of Fe-Ti oxide minerals were determined by the electron probe microanalyzer of Akita University (Model JEOL JXA-5 with 40° take-off angles). Analytical conditions are as follows: accelerating potential of 15 kV, beam current of 0.02 μA on Zn₂SiO₄. Analyses were made for elements Ti, Fe, Mn, and Mg using natural and synthetic oxides as standards. The correction was
made by the \(\alpha\)-factor method (Bence and Albee, 1968) using \(\alpha\)-factors by Albee and Ray (1970).

The composition of ilmenite varies considerably in the components \(\text{FeTiO}_3\), \(\text{Fe}_2\text{O}_3\), and \(\text{MnTiO}_3\) (Table 2; Text—fig. 13). Ilmenite contains 15-34 mol. % \(\text{MnTiO}_3\) and 5-7 mol. % \(\text{Fe}_2\text{O}_3\) in the Ohbisagawa-type GD, and 6-17 mol. % \(\text{MnTiO}_3\) and 1-9 mol. % \(\text{Fe}_2\text{O}_3\) in the Yaguki-type GD. The Yokokawa-type GD contains 8-12 mol. % \(\text{MnTiO}_3\) and 2-5 mol. % \(\text{Fe}_2\text{O}_3\). Ilmenite in the Ohbisagawa-type GD has the greatest enrichment in \(\text{MnTiO}_3\) among these granodiorites. Ilmenite in the magnetite-bearing rocks within the Yaguki-type GD has relatively higher contents of \(\text{MnTiO}_3\) (11-16 mol. %; mean 14 mol. %) and \(\text{Fe}_2\text{O}_3\) (3-9 mol. %; mean 7 mol. %) in comparison with the magnetite-free rocks.

Table 2 Representative chemical compositions of magnetite and ilmenite from the granodiorites around the Yaguki mine as determined by EPMA.

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* \(\text{FeO}\) and \(\text{Fe}_2\text{O}_3\) as calculated from charge balance on given number of sites after Stormer (1983).

** Recalculated mole fractions of ulvöspinel (Xusp) and ilmenite (Xilm).

*** Calculated temperatures and oxygen fugacities after Spencer & Lindsley (1981).

1-7: Yaguki-type granodiorite
8-9: Ohbisagawa-type granodiorite
10-11: Yokokawa-type granodiorite
Magnetite in the Yaguki-type GD contains little or no Mn and only small amounts of Ti; the highest ulvöspinel molecular content is 7 mol. % with most values being less than 5 mol. %.

Distribution of MnO contents of ilmenite within the Yaguki-type granodiorite body

The MnO content of ilmenite from the Yaguki-type GD ranges from 2 to 8 mol. % and the distribution pattern of it within the body tends to show a NS-trend (Text-fig. 14). High concentrations of MnO in ilmenite (more than 7 mol. %) are observed in the western part of the body (the Nambu-Hinokiyama area) where magnetite-bearing type occurs. Ilmenite has relatively lower MnO contents in the central part (3-5 mol. %) and eastern side of the body (less than 3 mol. %). MnO contents in ilmenite within the body tend to increase toward the west as a whole. This distribution pattern is apparently not in harmony with that of alkali contents based on the whole rock chemistry.
Chlorine and fluorine contents in apatite

Apatite observed in the three types of granodiorite occurs as euhedral to subhedral prismatic grains which are usually included in biotite and hornblende, and partially in plagioclase and quartz. Apatite ranges from 5 to 300 microns in diameter with an average size of about 60 microns.
Analytical Procedure

Chemical compositions of apatite were determined by the electron probe microanalyzer as described before. Measured spectra are; CaKα (analyzing crystal: PET, standard material: CaSiO₃), PKα (PET, apatite), FKα (RAP, topaz), CIKα (PET, pyrosmalite). Analytical conditions are an accelerating potential of 15 kV with a beam current of 0.08 μA on Zn₂SiO₄ for FKα and 0.02 μA for others, and beam diameter of 5 microns. Relative intensity ratios of the sample and the standard on the peak position were measured for Ca, P, and Cl. Integrated intensities of both sample and standard were measured for fluorine because the peak profile of FKα of apatite does not correspond with that of topaz. These relative intensity ratios were converted into oxide percentages by the α-factor method (Bence and Albee, 1968) using the α-factors by Albee and Ray (1970). H₂O content in apatite is calculated by assuming F+Cl+OH=2.0 in structural formula.

Chlorine and Fluorine contents of apatite

Table 3 shows representative data of CaO, P₂O₅, Cl, and F contents for apatite in individual rock types, and chlorine and fluorine contents are plotted in Text-fig. 15. Apatite in the Yaguki-type GD has 1.9-3.5 wt. % F, 0.04-0.5 wt. % Cl with Cl/OH=0.15 (atomic ratio), and in the Ohbisagawa-type GD 1.8-3.0 wt. % F and 0.1-0.4 wt. % Cl, while in the Yokokawa-type GD has 2.2-3.5 wt. % F and lesser amount of Cl (less than 0.1 wt. %).

Fluorine and chlorine contents of apatite in the Yaguki-type GD are plotted against D. I. of the host rocks (Text-fig. 16). Although apatite in the Yaguki-type GD exhibits rather great range of fluorine content, even within individual specimens, fluorine content does not greatly change with an increase in the D. I. of the host rocks. On the other hand, chlorine contents of apatite in the Yaguki-type GD slightly increase with increasing D. I. in the early stage of magmatic differentiation (D. I.=64-68), and then decrease in the later stage (D. I.>68).

Fluid inclusions in the Yaguki-type granodiorite

Fluid inclusions in the Yaguki-type GD are mainly observed in quartz and occasionally in plagioclase and biotite. Most of the fluid inclusions show a tiny round shape up to 10 microns, but negative crystal occasionally occurs. Fluid inclusions in euhedral plagioclase is less in number than those in anhedral quartz crystals. Some fluid inclusions occur along the cracks of host minerals, and these fluid inclusions might be secondary inclusions. They are classified into the following three types according to the volumetric proportion of vapor and liquid, and whether the fluid inclusions contain solid phases at room temperature or not. However, homogenization temperatures were not determined. Type I are liquid-dominant two-phase inclusions containing a small to moderate vapor bubble. Type II are two-phase inclusions containing a moderate to large vapor bubble. Type III
## Table 3: Chemical compositions of apatite from the granodiorites around the Yaguki mine as determined by EPMA.

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<th>2 YO-05</th>
<th>3 OH-07</th>
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<td>99.08</td>
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<td>101.26</td>
<td>100.26</td>
<td>99.69</td>
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Numbers of ions on the basis of 26(O, OH, F, Cl)

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<th>11 Y3001</th>
<th>12 Y3008</th>
<th>13 Y0105</th>
<th>14 Y0207</th>
<th>15 Y0302</th>
<th>16 Y0303</th>
<th>17 Y0304</th>
<th>18 Y0507</th>
<th>19 YG-49</th>
<th>20 YG-54</th>
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<td>53.95</td>
<td>54.50</td>
<td>55.60</td>
<td>54.95</td>
<td>56.18</td>
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<td>P₂O₅</td>
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<td>42.82</td>
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<td>43.00</td>
<td>42.46</td>
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<td>42.49</td>
<td>42.79</td>
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<td>F</td>
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<td>2.79</td>
<td>3.32</td>
<td>2.58</td>
<td>2.94</td>
<td>2.61</td>
<td>2.22</td>
<td>2.52</td>
<td>2.94</td>
<td>3.11</td>
</tr>
<tr>
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<td>0.15</td>
<td>0.40</td>
<td>0.47</td>
<td>0.24</td>
<td>0.16</td>
<td>0.37</td>
<td>0.04</td>
<td>0.29</td>
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<tr>
<td>(H₂O)*</td>
<td>0.57</td>
<td>0.43</td>
<td>0.12</td>
<td>0.44</td>
<td>0.32</td>
<td>0.53</td>
<td>0.64</td>
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<td>0.27</td>
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<td>101.62</td>
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<td>O=F, Cl</td>
<td>1.08</td>
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<td>1.49</td>
<td>1.19</td>
<td>1.29</td>
<td>1.14</td>
<td>1.02</td>
<td>1.07</td>
<td>1.30</td>
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<td>Total</td>
<td>99.58</td>
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<td>99.96</td>
<td>99.25</td>
<td>99.17</td>
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<td>99.65</td>
<td>101.06</td>
<td>100.31</td>
<td>100.28</td>
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</table>

Numbers of ions on the basis of 26(O, OH, F, Cl)

*H₂O calculated on the basis of 2(OH, F, Cl) per formula unit.

1-2: Yokokawa-type granodiorite
3-4: Ohbisagawa-type granodiorite
5-20: Yaguki-type granodiorite

*H₂O calculated on the basis of 2(OH, F, Cl) per formula unit.
Text-fig. 15 Chlorine and fluorine contents in apatite of granodiorites around the Yaguki mine.

Text-fig. 16 Variation diagrams of fluorine (upper) and chlorine (lower) contents in apatites of the Yaguki-type granodiorite with D. I. of the host rocks. Bar indicates standard deviation.
are three-phase inclusions having liquid, a vapor bubble, and solid. Solid phases might be almost halite, sylvite, and unknown transparent and opaque minerals. An occurrence of halite at room temperature in type III means that the salinity is higher than about 26 wt. % (NaCl equivalent) in those inclusions. Euhedral plagioclase has a small number of tiny fluid inclusion, but the quantity ratio of type III to type I is higher than that of anhedral quartz. Fluid inclusions in anhedral quartz consist mainly of type I, however some of them consist of type III. Type II is rare in both euhedral plagioclase and anhedral quartz.

Discussions

Behavior of water in magma during magmatic differentiation

In the Yaguki-type GD, chlorine contents of apatite slightly increase with an increase of D. I. in the early stage of magmatic differentiation (D. I. = 64-68) and then decrease to the later stage (D. I. > 68) (Text-fig. 16). If distribution coefficient of chlorine between a magma and apatite has not greatly changed during magmatic differentiation, chlorine contents of apatite may be governed by that of residual magma. Decrease in chlorine in magma may be caused by crystallization of chlorine-bearing minerals and/or by partition of chlorine into aqueous fluid coexisting with magma (Anderson, 1974). Fluorine and chlorine are found in hydrous phase minerals such as biotite, hornblende, and apatite in the Yaguki-type GD. The substitution of F for OH is much easier than that of Cl for OH in crystal lattices of hydrous minerals (Stormer and Carmichael, 1971), and so if the magma is crystallized without aqueous fluid (unsaturated with water), consumption of chlorine in magma may not be greater than that of fluorine with crystallization of hydrous minerals. In the Yaguki-type GD, chlorine contents of such minerals are not so high (e.g. biotite: Cl = 0.16-0.21 wt. %; Fujikawa, unpublished data), and the modal abundance of these minerals does not change abruptly at about D. I. = 68. Therefore, crystallizations of these minerals might not act on extraction of chlorine from magma in the Yaguki-type GD.

Kilinc and Burnham (1972) showed the ratio of the chlorine content in silicate melt to that in coexisting aqueous fluid as a function of pressure. The pressure during the solidification of Yaguki-type GD is estimated to be about 1.5 kilobars, as described before, if water pressure is nearly equal to the total pressure. Based on the FeS contents (17.8-18.9 mol. %) in sphalerite coexisting with hexagonal pyrrhotite and pyrite, as determined by electron probe analysis, the estimated pressure of the mineralization at the Akahage ore body in the Yaguki-type GD is 1.3-2.1 kilobars (Table 4). Shimizu and Shimazaki (1981) also concluded that the formation pressure of this deposit using a sphalerite geobarometer was 1.5 kilobars (Table 4). At 1.5 kilobars pressure, the chlorine molality in the aqueous fluid is about 33 times that in the silicate melt (Kilinc and Burnham, 1972). If the magma is saturated with water and is associated with aqueous fluids, chlorine is concentrated into aqueous fluids and the activities of chlorine in the residual magma may
Table 4  The total pressures estimated by means of Hutchison and Scott (1981) and chemical compositions of sphalerite associated with hexagonal pyrrhotite and pyrite from the Akahage ore body, the Yaguki ore deposit.

<table>
<thead>
<tr>
<th></th>
<th>Weight percent</th>
<th>FeS mole %</th>
<th>Estimated Pressure (kb)</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Zn  Fe Mn Cd Cu</td>
<td>Total</td>
<td></td>
</tr>
<tr>
<td>Akahage ore body (425 mL)</td>
<td>54.0 11.3 0.1 2.9 0.9</td>
<td>32.2 101.4</td>
<td>18.9 1.3&gt;1.7(Av.)</td>
</tr>
<tr>
<td></td>
<td>54.8 10.4 0.1 2.0 0.1</td>
<td>32.7 100.1</td>
<td>17.8 2.1</td>
</tr>
<tr>
<td>Shimizu and Shimazaki (1981)</td>
<td></td>
<td>18.6</td>
<td>1.5</td>
</tr>
</tbody>
</table>

decrease. Namely, decrease in chlorine contents in Yaguki-type GD could have led to the partition of chlorine into aqueous fluid. The presence of high salinity fluid inclusions in the Yaguki-type GD support the above theoretical consideration that the differentiated magma of the Yaguki-type GD could have coexisted with aqueous fluids with high chlorine concentrations. Based on the assumption mentioned above, the magma of the Yaguki-type GD is initially unsaturated with water and becomes saturated (with water) with progress of crystallization. Finally, the magma of the Yaguki-type GD coexists with aqueous fluids at a later stage. As mentioned previously, the primary fluid inclusions in anhedral quartz are more abundant than those in euhedral plagioclase. This fact suggests that the activity of aqueous phase has been much greater in the later stage of magmatic differentiation than in the early stage, and this agrees with the behavior of aqueous fluid which is estimated by chlorine content in apatite.

Similar behavior of chlorine in apatite was reported in the Orikabe granitic rocks (Nedachi, 1974) and in the Matsumae plutonic rocks (Tsuchiya, 1986). Nedachi (1974) and Tsuchiya (1986) also concluded that these behavior had been caused by water saturation of magma.

Oxidation state

Oxidation states of the magma of the Yaguki-type GD is discussed on the basis of the chemical compositions of magnetite and ilmenite. Spencer and Lindsley (1981) showed that the chemical composition of coexisting magnetite and ilmenite were a function of oxygen fugacity and temperature. Chemical compositions of magnetite and ilmenite suggest that the magnetite-bearing type of the Yaguki-type GD might be solidified under the condition of slightly higher oxygen fugacity than NNO buffer line (T=550-650°C, fO2=10^{-19.5}-10^{-18.5} atm).

Text-fig. 17 shows the relationship between D. I. and MnO content in ilmenite of the Yaguki-type GD. The MnO content of ilmenite does not greatly change with an increase in D. I. of the host rock. However, there is a difference in the MnO content of ilmenite between the magnetite-bearing type (high MnO) and the magnetite-free type (low MnO) of the Yaguki-type GD. There is no difference in the bulk rock chemistry, the mode of occurrence, and textural characteristics
between them. These facts suggest that differences in the MnO content of ilmenite between the magnetite-bearing and the magnetite-free types does not depend on differences in the parent magma and the degree of magmatic differentiation.

Czamanske and Mihalik (1972) presented a model for the formation of Mn-rich ilmenite in oxidizing magma systems. Because Fe$^{2+}$ is more easily oxidized than Mn$^{2+}$ under the relatively higher oxygen fugacity, iron may be expelled from the ilmenite structure and ilmenite may be enriched in Mn. The magnetite-bearing rocks of the Yaguki-type GD might be solidified under the condition of relatively higher oxygen fugacity than the magnetite-free rocks. Ishihara (1977) showed that the formation of two different granitoids, the magnetite-series and the ilmenite-series, could be explained by a common original magma with different oxidation states. Namely, the magnetite-series granitoids were formed under conditions of higher oxygen fugacity than the ilmenite-series (Ishihara, 1971; Shimazaki, 1976). This supports the estimation of oxidation state discussed above in the Yaguki-type GD. MnO content in ilmenite within the Yaguki-type GD body tends to increase toward the west as a whole (Text-fig.14). It seems that oxygen fugacity of the Yaguki-type GD might increase toward the west, and the distribution pattern of oxygen fugacity does not agree with that of magmatic differentiation (Text-fig.10). Czamanske and Wones (1973) suggested that H$_2$O, separated from magma, can play as an oxidizing medium through dissociation and loss of H$_2$. In the Yaguki-type GD, separation of an aqueous fluid might not act as an oxidizing medium because there is no clear correlation between MnO content in

Text-fig. 17 Variation diagram of MnO contents in ilmenite of the Yaguki-type granodiorite with D. I. of the host rocks.
Text-fig. 18 Distribution map of the ore bodies at the Yaguki ore deposit with the surface structure of the Yaguki-type granodiorite body. Contour lines are the same as for Text-fig. 3.
ilmenite (oxidation state) and chlorine content in apatite (behavior of H₂O in magma).

Distribution of the ore bodies and nature of the granitoids
Ogawa and Shida (1975) and Shoji et al. (1975) emphasized that the distribu-

Text-fig. 19 Distribution map of chlorine contents in apatite within the Yaguki-type granodiorite body.
tion of the ore bodies in the Yaguki ore deposit are governed by geologic structures. The skarn zone and ore body at the No.1 ore body tend to occur along with NS-N30°E trending fissures associating with the formation of the No.1 dome structure (Ogawa and Shida, 1975). Furthermore, the ore bodies are localized in the trough of the syncline and at the top of the dome structure (Shoji et al., 1975). Based on the surface structure of the Yaguki-type GD, the ore bodies are distributed around local domes which were formed by the intrusion of the Yaguki-type GD (Text-fig. 18).

Text-fig. 19 shows the distribution of chlorine content in apatite within the Yaguki-type GD body. This distribution pattern is similar to that of the magmatic differentiation (Text-fig. 10). Furthermore, the ore bodies tend to be distributed in the places where chlorine content in apatite is lower. These facts suggest that not only the geologic structure but also the nature of the magma might control the distribution of ore bodies in the Yaguki ore deposit. Namely, the ore mineralization occurred near the magma of the Yaguki-type GD coexisting with high salinity aqueous fluid. Holland (1972) suggested that base metals in silicate melts are strongly partitioned into the aqueous fluid coexisting with silicate melts of granitic composition, and that the partition ratio is roughly proportional to the square of the chloride concentration in the aqueous fluid.

Accordingly we have come to the following conclusions on the genesis of magma and mineralization: Magma of the Yaguki-type GD was initially unsaturated with water, but it became saturated with water during magma crystallization. Finally the magma coexisted with an aqueous fluid at a later stage. The chlorine content in apatite is lower. These facts suggest that not only the geologic structure but also the nature of the magma might control the distribution of ore bodies in the Yaguki ore deposit. Namely, the ore mineralization occurred near the magma of the Yaguki-type GD coexisting with high salinity aqueous fluid. Holland (1972) suggested that base metals in silicate melts are strongly partitioned into the aqueous fluid coexisting with silicate melts of granitic composition, and that the partition ratio is roughly proportional to the square of the chloride concentration in the aqueous fluid.

Accordingly we have come to the following conclusions on the genesis of magma and mineralization: Magma of the Yaguki-type GD was initially unsaturated with water, but it became saturated with water during magma crystallization. Finally the magma coexisted with an aqueous fluid at a later stage. The chlorine

![Text-fig. 20 Schematic model on the relationship between the sites of ore bodies and the nature of magma at the Yaguki ore deposit. Xls: crystallized minerals from silicate melt; L: silicate melt; V: aqueous fluid coexisting with silicate melt.](image-url)
and base metals in the magma were strongly partitioned into the aqueous fluid which was mainly composed of H₂O. The aqueous fluid escaped from the granodioritic magma and then moved up to the sedimentary rocks through the fissure zones. Mineralization occurred at the boundary between the slate and limestone beds in the Yaguki ore deposit.

However, the genetic relationship between the copper-iron and the tungsten ore mineralizations still remains an unsolved problem from the viewpoint of granitic magmatism. Further detailed investigations should be done on the genesis of the ore mineralization in the skarn zone. A schematic model on magmatic and ore genoses at the Yaguki ore deposit is depicted in Text-fig. 20 based on the above discussion.

Acknowledgments

Some of the results reported here are taken from the work carried out at Akita University, the work having been completed at Hokkaido University. We are very grateful to Prof. Yohei Ishikawa and Dr. Daizo Ishiyama of Akita University for their excellent guidance and support. We would like to acknowledge the guidance and encouragement of Prof. Shunzo Yui of Hokkaido University. We are also much indebted to Mr. Tsugio Hirano of Akita University for carrying out chemical analyses. Mr. Kenichi Takizawa of the Nittetsu Mining Co., Ltd. and the staff of the Shin-Yaguki mining Co., Ltd. gave us kind support and advice during our field work.

References


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