

# Etch Figure Patterns of Magnetite from Skarn Deposits in Japan

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## Abstract

Magnetites from skarn type deposits in Japan were cut, polished and etched, and etched surfaces were examined for textural types of etch figures. Various types of etched figures occur, and distinct patterns are associated with magnetites from distinct deposits. The figures are roughly classified into etch pits and zonings. The etch pits almost always appear on the polished surfaces of magnetites from several deposits. Etch pits are attributed to lattice defects or the presence of minor elements. The zoning patterns are observed in magnetites from several other deposits. The zoning patterns reflect multistage mineralization during skarn formation. For the Akaiwa deposit, zoning in magnetites are related to a shift from metasomatic to hydrothermal mineralization. These etch figures can be sensitive indicators of fluctuations of ore forming environments.

Keywords; magnetite, etch figure, skarn deposit

## 1. Introduction

Iron skarn type ores almost always contain massive magnetite. Hence, skarn deposits were an important iron resource in Japan. Etching is a method that emphasizes small differences in structures inside minerals. These structures could be due to variations during initial crystallization, or post-crystallization events. We have reported previously that diverse etch figures occur in magnetites derived from various rock types, including skarn deposits (Sekiguchi and Enjoji, 2009). In this study, magnetites from the representative iron skarn deposits in Japan were etched and the diverse etch figure patterns associated with different deposits are discussed.

## 2. Samples and Geological Settings

Magnetite crystals provided for this study are from 6 ore deposits of 5 mines. These are pyrometasomatic deposits of representative iron (and others) skarn type in Japan (Fig. 1). These mines were formerly mined for iron and other metals; however all the mining operations of ore mining are closed at present. All of ore samples consist mainly of massive magnetite accompanied by small quantities of other minerals.

1) The Shin-yama deposit of the Kamaishi mine (Fig. 2a, b)

The Kamaishi mine is located at Iwate Prefecture, northeastern Japan (Fig. 1), and was

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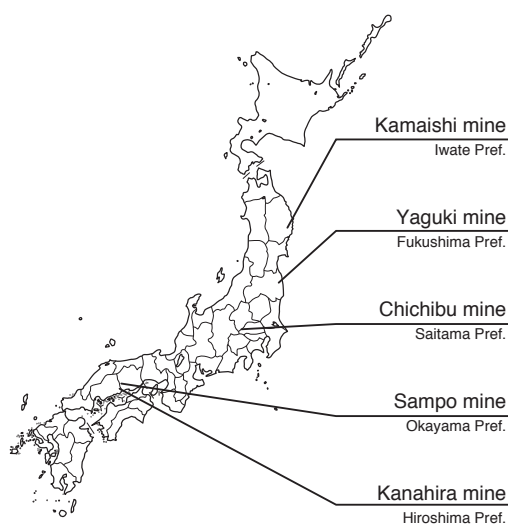


Fig. 1. Location map of the mines investigated.

mined for iron and copper. The mine has more than a dozen ore deposits. They are iron and/or copper ore and the ores are mainly composed of magnetite and/or chalcopyrite.

The area of the Shin-yama deposit consists mainly of the Mesozoic to Paleozoic sedimentary formations and the Ganidake igneous complex of Early Cretaceous age (Hamabe and Yano, 1976). Many deposits including the Shin-yama deposit are distributed around the Ganidake igneous complex. The Shin-yama deposit was formed along the boundary between diorite to diorite porphyry of the Ganidake igneous complex and the Nagaiwa-Onimaru limestone of Middle to Upper Carboniferous age (Hamabe and Yano, 1976). The ore bodies occur in the garnet dominant skarn and principal minerals of the skarn are grandite garnet, clinopyroxene and epidote, accompanied by minor tourmaline, axinite, vonsenite, amphibole, wollastonite and microcline (Hamabe, 1979). The ore samples from the Shin-yama deposit are mainly composed of magnetite, with some chalcopyrite and pyrite.

## 2) The Sahinai deposit of the Kamaishi mine (Fig. 2c, d)

The Sahinai deposit of the Kamaishi mine is located at about 1 km from the Shin-yama deposit described above. The regional geologic setting is the same as for the Shin-yama deposit. The Sahinai deposit produced iron ore. The Sahinai deposit occurs in a sheet-like body in the garnet dominant skarn nearest the Ganidake igneous rocks (Hamabe, 1979). The ore samples from the Sahinai deposit are mainly composed of magnetite, accompanied by minor chalcopyrite and pyrite.

## 3) The Hinoki-yama deposit of the Yaguki mine (Fig. 2e, f)

The Yaguki mine is located at Fukushima Prefecture, northeastern Japan (Fig. 1), and was mined for iron, copper and tungsten. The area of the deposit consists of Paleozoic sedimentary formations and several igneous rocks. The ore bodies of the deposits are found in the Carboniferous Yaguki Limestone, which consists of slate and limestone (Fujikawa and Matsueda, 1991). It is inferred that ore mineralization of the deposits was related to intrusion of the Yaguki-type granodiorite (Ogawa and Shida, 1975). K-Ar ages indicate that the mineralization of the granodiorite is Early to Middle Cretaceous (Kawano and Ueda, 1967). Apparently, two types of ore mineralization occurred, resulting in copper-iron-rich and the tungsten-rich mineralized bodies. Fluid inclusions suggest that the tungsten mineralization event might have occurred later than the copper-iron mineralization (Muramatsu and Nambu, 1982).

The skarn occurs along the boundary between limestone and slate beds in the Yaguki Limestone, and is mainly composed of garnet, clinopyroxene, epidote and amphibole (Fujikawa and Matsueda, 1991). The copper-iron ore bodies are embedded in the skarn zone, especially in the garnet skarn

(Fujikawa and Matsueda, 1991). The ore samples from the copper-iron ore of the Hinoki-yama deposit are mainly composed of magnetite, accompanied by chalcopyrite and pyrrhotite.

4) The Akaiwa deposit of the Chichibu mine  
(Fig. 3a, b)

The Chichibu mine is located at Saitama Prefecture, central Japan (Fig. 1), and was mined for iron, copper, lead, zinc, gold, silver and manganese. The regional geology of the area of the deposit is dominated by the Paleozoic Nakatsugawa group and a Miocene quartz diorite. The Carboniferous Ishibune formation belongs to the Paleozoic group and is the host rock of the deposit. The Ishibune formation consists of massive sandstone, slate, limestone and chert (Ueno and Tonouchi, 1987).

The ore deposits of the mine occur mostly in limestone of the Ishibune formation. The ores are mainly composed of magnetite, pyrrhotite, pyrite, sphalerite, galena, chalcopyrite, arsenopyrite and hematite, and the skarns are composed of garnet, clinopyroxene, epidote, actinolite, vesuvianite, ilvaite and wollastonite (Miyazawa *et al.*, 1970). Types of mineralization in the Akaiwa deposit are divided into a pyrometamorphic type in early stages and a hydrothermal metasomatic type in later stages (Kaneda and Watanabe, 1961). The ore samples from the Akaiwa deposit consist mainly of porous magnetite, accompanied by pyrite and minor abundances of other minerals.

5) The Yoshiki deposit from the Sampo mine  
(Fig. 3e, f)

The Sampo mine is located at Okayama Prefecture, western Japan (Fig. 1), and was mined for iron and copper. The area of the deposit consists of Permian limestone, intruding by late Cretaceous biotite granite. The mine consists

of two deposits, the Yoshiki deposit worked for iron and copper, and the Arayama deposit mined for iron. The Yoshiki deposit was formed at the contact between calcite-marble belonging to Permian Nakamura Limestone and a leucocratic biotite granite (Yoshida, 1961). The skarns are formed by the replacement of limestone (calcite-marble) and slate (pelitic hornfels), and principal minerals of the skarn are clinopyroxene, garnet (andradite-grossularite), lieverite, wollastonite, fluor spar, quartz and calcite (Ogawa, 1975). The ore samples from the deposit are mainly composed of magnetite, accompanied by chalcopyrite and pyrite.

6) The Kuryu-dani deposit of the Kanahira mine  
(Fig. 3c, d)

The Kanahira mine is located at Hiroshima Prefecture, western Japan (Fig. 1), and was mined for iron. The area of the deposit consists of Permian limestone and Cretaceous rhyolite (Harada, 1984). The skarn of the mine is composed of garnet, diopside, hedenbergite, wollastonite (Harada, 1984). The Kuryu-dani magnetite occurs as anhedral crystals, which are texturally distinct from the euhedral magnetite from the Sampo mine. The ore samples from the Kuryu-dani deposit are mainly composed of magnetite, with minor pyrrhotite.

### 3. Methods

The specimens were cut to the proper size, ground, and finally polished using 0.04  $\mu\text{m}$  colloidal silica. The magnetite crystals have massive forms, so it was not possible to orient crystal faces for etching.

The agent used for etching is hydrochloric acid solution. Specimens are immersed into the agent in a pressure-resistant container with temperature held at 100 °C. The degree of etching is highly

dependent on sample locality and the direction of crystal faces. Thus the suitable concentration of agent and the etching period were tested repeatedly. The previous etching experiments of Aoki and Iwasaki, (1980) were carried out at room temperatures and using an agent of high concentration, higher than several mol/l. These conditions result in such heavily etched surfaces that contrasts in etching figures can be difficult to observe. For this experiment, dilute hydrochloric acid (less than 1 mol/l), and higher temperature were used. The etching period is approximately 3 to 6 hours. By these conditions, clear etching figures were obtained. Etch figures were observed using a differential interference microscope.

#### 4. Results and Consideration

Various etching figures occur on the polished surfaces of the magnetites of this study. Many of the etching figures are characteristic of magnetites from specific deposits, and appear to be related to their genesis (Fig. 2, Fig. 3). The exposed etch figures observed are classified into zonings and etch pits.

Etch pits were observed on almost all of the etched surfaces of magnetite. However, abundances of pits differ among the crystals from different deposits. For magnetite from the Kanahira mine, zones of high-densities of pits and low densities of pits are observed in individual crystals (Fig. 3f). High densities of etch pits are generally attributed to high densities of lattice defect. The results for the Kanahira mine suggest that the stresses during and after crystal growth caused various concentrations of defects. Alternatively, etch pits may be due to an intercalation of minor elements. Sekiguchi and Enjoji (2012) reported that the magnetites from skarn ore deposits almost always contain minor elements, such as silica, aluminum, magnesium, and others.

Growth zonings were dominantly observed on magnetite from the Sahinai deposit (Fig. 2a, b) and the Shin-yama deposit (Fig. 2c, d) of the Kamaishi mine and the Akaiwa deposit (Fig. 3a, b) of the Chichibu mine. Zoning patterns revealed by etching are generally derived from environmental variations during crystal growth. The zoning patterns observed in this study have characteristic structures that correlate with different deposits. The zoning patterns of magnetite from the Sahinai deposit form linear uneven steps with growth hillocks (Fig. 2a). Regarding the magnetite from the Shin-yama deposit, the zoning pattern consists of the etch pits arranged in lines (Fig. 2d). Some zoning patterns take on different structures between core and rim (Fig. 2b, 3a). This aspect suggests a drastic variation of the ore-forming environment, or else a gap of time in crystal growth. A growth zoning is likely formed by an epitaxial growth with variable transporter like a hydrothermal fluid. In contrast, there are no etch figures in magnetites which crystallize at high temperatures such as in igneous rocks (Sekiguchi and Enjoji, 2009). In fact, skarn forming mineralization of the Akaiwa deposit of the Chichibu mine is divided into an early metasomatic stage and a later hydrothermal stage (Kaneda *et al.*, 1961). This is consistent with the zoned etch figures of the Akaiwa magnetites (Fig. 3a).

Magnetites from the Yaguki mine and the Sampo mine showed no etch figures. From the Yaguki mine, minute holes similar to etch pits are scattered on the etched surface (Fig. 2f); we attribute these holes to tiny mineral inclusions that were removed by etching.

#### 5. Conclusion

In this study, diverse etch figures were identified on magnetite crystals from skarn deposits. Different



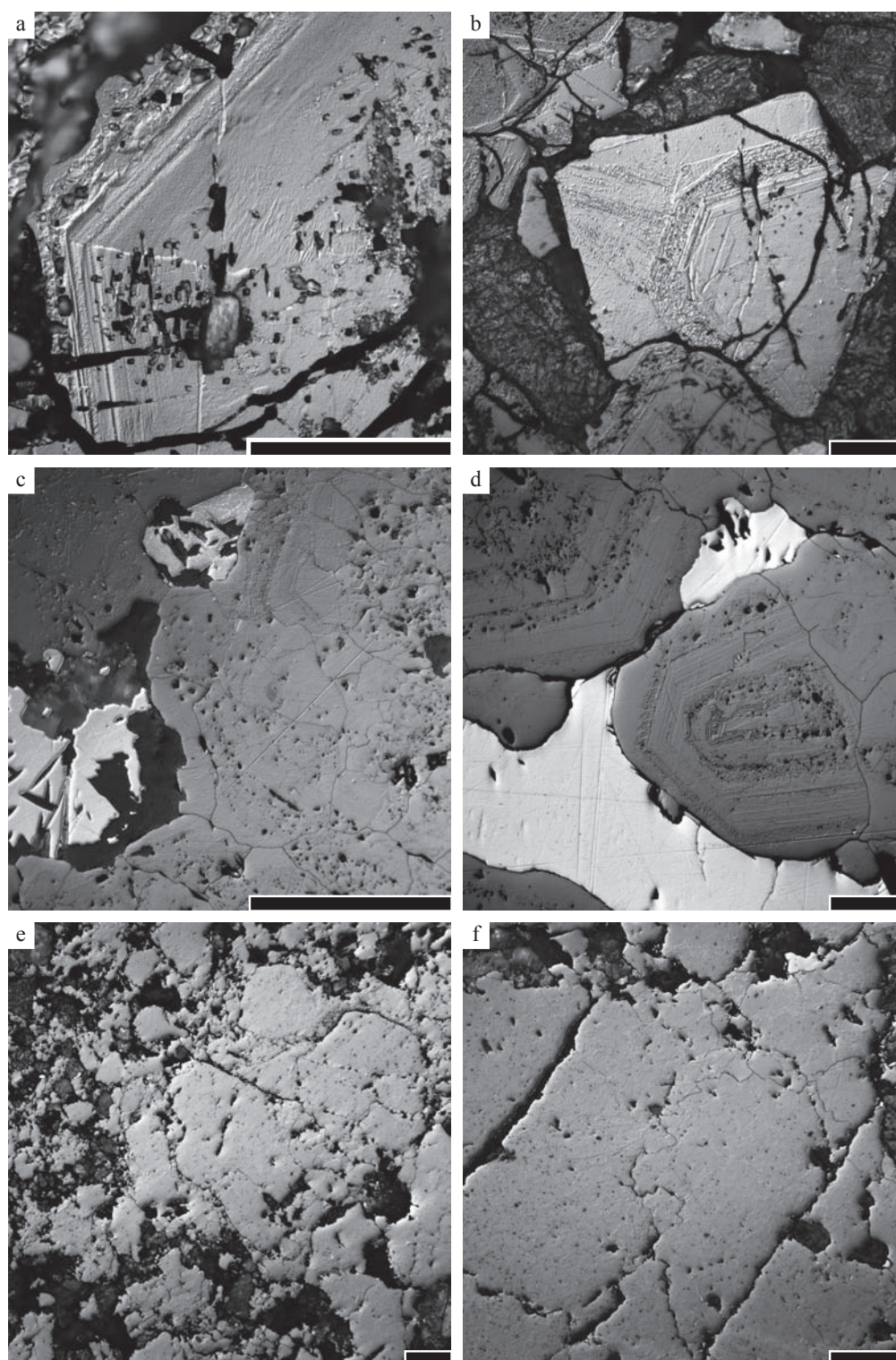


Fig. 2. Etch figures. a) and b): Magnetite from the Sahinai deposit of the Kamaishi mine. Growth zoning patterns are observed. c) and d): Magnetite from the Shin-yama deposit of the Kamaishi mine. Growth zoning patterns are observed, which seemed to be composed of etch pits in (d). e) and f): Magnetite from the Hinoki-yama deposit of the Yaguki mine. Etched surfaces are smooth and show no particular etched structure. Scale bars show 100  $\mu\text{m}$ . All images are taken by the differential interference microscope.



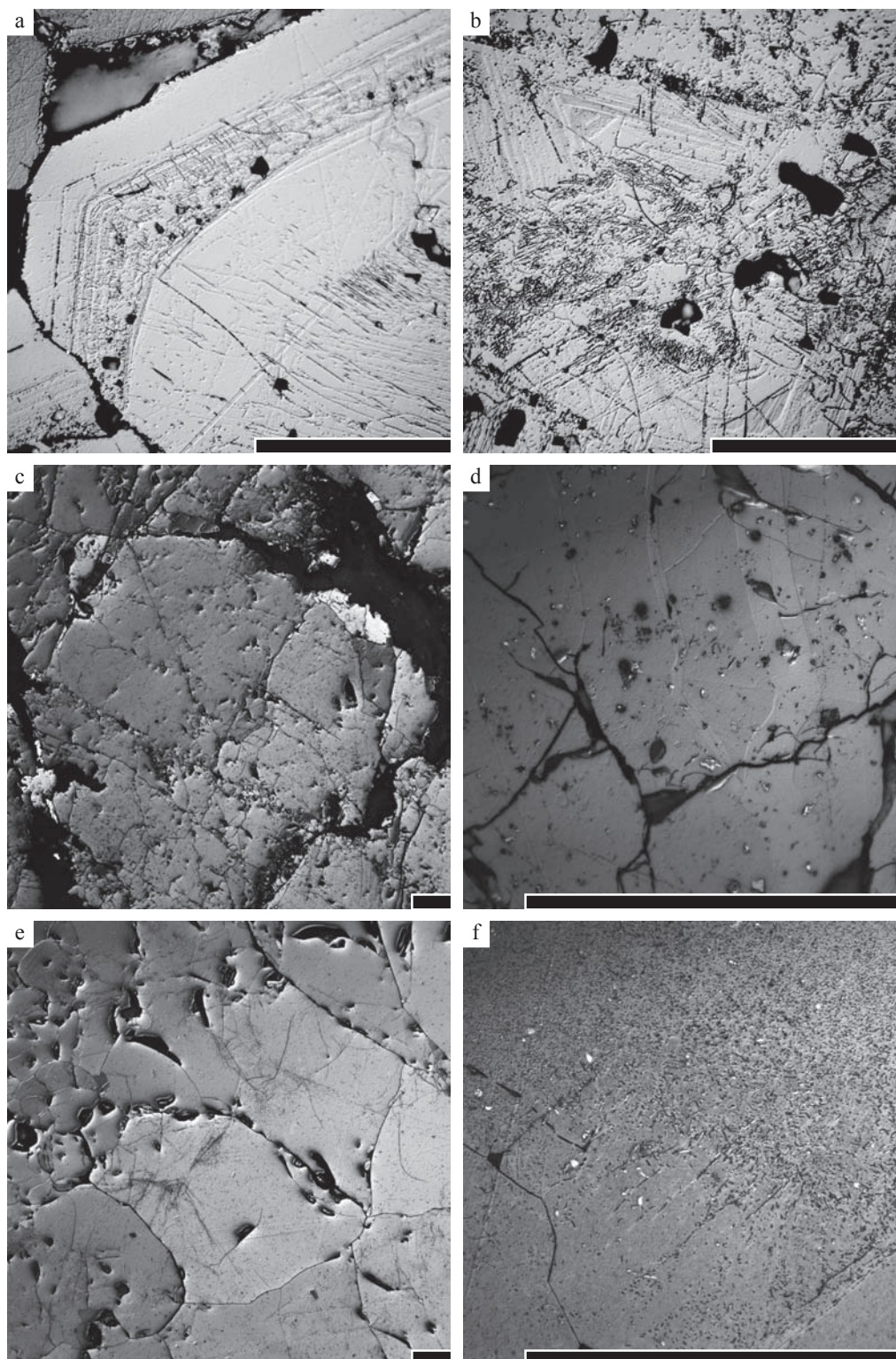


Fig. 3. Etch figures. a) and b): Magnetite from the Akaiwa deposit of the Chichibu mine. Growth zonings and etch pits are observed. c) and d): Magnetite from the Yoshiki deposit of the Sampo mine. Etched surface is smooth and there is no etched structure. e) and f): Magnetite from the Kuryu-dani deposit of the Kanahira mine. A single surface shows different densities of etch pits (f). Scale bars show 100  $\mu\text{m}$ . All images are taken by the differential interference microscope.

types of etch figures are associated with different deposits. Skarn deposits almost always contain magnetite as massive forms, however, etching reveals more information regarding crystal growth than can be found from the minerals without etching. This study revealed internal structures in magnetite, which had not been discussed previously.

It is known that skarn type deposits are often formed with several stages of metasomatic mineralization. Etch figures show evidence of these stages as growth zoning textures on magnetite surfaces from several deposits. Etch figures also may reflect a fluctuation of an ore forming environment, such as temperature, pressure, chemical compositions of ore-forming fluid, speed of mineralization. Because of the common occurrence of magnetite in skarn deposits, study of etched magnetite surfaces can help in tracing of mineralization in skarns, and furthermore lead to a better understanding of the genesis of ore formation.

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