Behavior of the Rare Earth Elements during the Skarn Formation at the Kamaishi Mine, Japan

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Abstract: The distribution and behavior of the REE in the zoned skarns of the Nippo and Shinya mine deposits, Kamaishi mine, are described. The zoned skarns are developed between dioritic rocks and limestone, and the REE abundances of skarns decrease from the dioritic rock side to the limestone side. All the skarns have lower REE contents than the dioritic rocks, implying that REE of the skarns were derived from the dioritic rocks, and no or little REE was added to the skarns from hydrothermal fluids. Clinopyroxenes show negative Eu anomalies on chondrite-normalized REE diagrams, and the magnitude of the Eu anomaly increases from the diorite side to the limestone side. Garnets and garnet skarns exhibit large variations in the extent of Eu anomaly. The oxygen fugacity (fo2) is the main factor that controls Eu\textsuperscript{+3}/Eu\textsuperscript{+2} ratios in the minerals; the negative Eu anomaly of clinopyroxene increases with a decrease of fo2, and garnet preferentially takes Eu\textsuperscript{+3} relative to Eu\textsuperscript{+2}. The fo2 of hydrothermal fluids had declined due to the metasomatic reaction with graphite-bearing limestone. The garnets with positive Eu anomalies were formed by the reaction between dioritic rocks and initial hydrothermal fluids with higher fo2. The garnets with negative Eu anomalies were produced by the reaction between limestone and the initial fluids, or between dioritic rocks and the secondary fluids with lower fo2. The secondary lower fo2 fluids were originated by the reaction of the initial fluids with limestone.

Introduction

Skarn deposits are commonly formed by metasomatic reaction essentially between hydrothermal fluids and limestone, which produce concentration and deposition of metallic elements. In the metasomatism of skarn, almost all elements including metallic elements are mobile on a large scale and form distinctive reaction zones. The mobility of major elements and ore-forming metallic elements in zoned skarn is discussed in some papers, but little is known on the abundance and mobility of the rare earth elements (REE) in the zoned skarn. Therefore it is valuable to know the behavior of the REE during the skarn formation. The REE are useful as tracer of geochemical processes, especially for determining the origin of igneous rocks, because of their unique chemical behavior. The REE behavior in ore formation processes is poorly understood, because most sulfide and oxide ore minerals are not good hosts for the REE, and there are limited data on REE partition coefficients between skarn minerals and fluids (ex. CULLERS and GRAF, 1984).

This paper describes the distribution and behavior of the REE in the zoned skarns of the Kamaishi mine. These skarns show large variations of REE patterns, reflecting their various modes of occurrence. Garnet, one of major skarn minerals, is a HREE-enriched host mineral and exhibits a widespread Eu anomaly. The purpose of this paper is to reveal relationships among the REE behavior, the geological condition and the mechanism of skarn formation in the Kamaishi mine.

General Geology

The Kamaishi mining district is underlain by sedimentary rocks of the Carboniferous, Permian and Early Cretaceous age and the Cretaceous igneous rocks. The igneous rocks consist mainly of diorite-diorite porphyry (quartz diorite in the Nippo deposit), the Ganidake granodiorite and the Kurihashi granodiorite, intruded in this order.
Fig. 1 Geological map of the western side ore deposits of the Kamaishi mine (HAMABE, 1979). The geological map is compiled from geological maps of the Shinyama 450-m level, Sahinai and Ohmine 725-m level, and Nippo 250-m level.

1: iron orebody, 2: iron-copper orebody, 3: copper orebody, 4: skarn, 5: slate and sandstone, 6: limestone, 7: andesitic pyroclastic rocks, 8: the Kurihashi granodiorite, 9: diorite and diorite porphyry, 10: the Ganidake granodiorite. Three circles represent studied areas in this paper.

Fig. 2 Geological sketch map of the zoned skarns on the 250-m level of the Nippo ore deposit.

The zoned skarns are composed of skarn I, II and III, listed from the quartz diorite to the limestone side (OCHIAI, 1987).
The former two plutons are distributed contiguously and called the Ganidake igneous complex. The K-Ar ages of the Ganidake granodiorite and the Kurishiai granodiorite are 119 Ma and 122 Ma, respectively (KAWANO and UEDA, 1965).

More than ten ore deposits are distributed in the eastern and western sides of the Ganidake igneous complex, especially of the Ganidake granodiorite. Large ore deposits are located in the western side, mainly replacing the Nagaiwa-Onimaru limestone of Carboniferous age, and called the Ohmine, Nippo, Sahinai and Shinyama ore deposits, from north to south. A geological map around the west side ore deposits district is shown in Fig. 1 (HAMABE, 1979). We investigated zoned skarns around the D4 orebody in the Nippo ore deposit, and the skarns around 4D and 2D orebodies in the Shinyama ore deposit. The Shinyama ore deposit is the largest iron and copper deposit in the Kamaishi mine, and the Nippo ore deposit is the largest copper deposit. On the basis of the distribution of the ore deposits around the complex and the high Cu, it is considered that the formation of the ore deposits is closely related to the Ganidake igneous complex (HAMABE and KUWAHATA, 1977).

Zonation and REE Patterns of the Skarns in the Nippo Ore Deposit

A geologic sketch map of the zoned skarn on the 250-m level of the Nippo ore deposit is shown in Fig. 2. The zoned skarn of about 50 m width, developed at the boundary between quartz diorite and limestone (crystalline limestone), is divided into skarn I (Ia and Ib), II and III from the quartz diorite side. OCHIAI (1977, 1987) and OCHIAI et al. (1987) reported petrological characteristics of the zoned skarn and clarified the behavior of major and trace elements in the skarn. The mineral assemblages of the quartz diorite and skarns are as follows; quartz diorite: hornblende+biotite+clinopyroxene + plagioclase + alkali feldspar + quartz, skarn Ia: plagioclase + hornblende + clinopyroxene + quartz + alkali feldspar, skarn Ib: plagioclase+clinopyroxene+quartz+alkali feldspar, skarn II: clinopyroxene + garnet + hornblende + plagioclase+calcite+quartz, skarn III: clinopyroxene+garnet+quartz. The skarn II is richer in garnet compared to the skarn III, whereas the skarn III in clinopyroxene. Judging from the rock texture and chemical compositions, the initial boundary between the quartz diorite and the limestone must have been located within the zone of skarn II. The skarn I and the skarn III are endomorphic and exomorphic, respectively. The zoned skarns were formed by metasomatic reaction along the contact between the quartz diorite and the limestone, promoted by the introduction of hydrothermal fluids (OCHIAI, 1987).

The REE were measured using an inductively coupled argon plasma emission spectrophotometer (ICP, Jarell Ash ICAP-575), following the technique of TAGIRI et al. (1989). Chondrite-normalized REE patterns of the zoned skarn are presented in Fig. 3. The REE abundance is the highest in the quartz diorite and decreases in the order of the skarn I, II, III and limestone. The REE patterns for the quartz diorite and the skarn I are similar to each other, showing moderate LREE enrichment and HREE depletion. The skarn II exhibits weak convex REE patterns with slight MREE enrichment. The skarn III is characterized by low REE content and negative Eu anomaly. The limestone has the lowest REE content and negative Eu anomaly. All the skarns except the...
Fig. 4 Chondrite-normalized REE patterns of clinopyroxenes from the zoned skarns of the Nippo ore deposit. The same symbols as in Fig. 3. Numbers correspond to Eu/Gd ratios representing the magnitude of negative Eu anomalies. The extent of negative Eu anomalies increases from the skarn I to the skarn III.

Fig. 5 Chondrite-normalized REE patterns of garnets from the zoned skarns of the Nippo ore deposit. The garnets in the skarn II exhibit small positive Eu anomalies, and those in the skarn III at the limestone side have large negative Eu anomalies.

Fig. 6 East-west geological section (N310) of the Shinyama 4D orebody (after the Kamaishi Mining Company, Ltd). The distribution area of the skarns enlarges from the lower 400-m level to the upper 600-m level.

Figures 4 and 5 show the skarn II show negative Eu anomalies.

On the basis of these REE analyses, followings are deduced. The REE were immobile at the replacement site of quartz diorite to skarn I. At the reaction site of skarn I to skarn II, the LREE such as La, Ce and Nd were removed to the external system, but MREE and HREE were preserved. The preservation of MREE and HREE in the skarn II is due to the presence of garnet, a HREE-enriched host mineral, as mentioned later. All the skarns have lower REE contents than the quartz diorite, implying that an addition of REE from hydrothermal fluids was insignificant. The skarn III contains low REE and shows negative Eu anomaly, reflecting its derivation from the limestone.

Figures 4 and 5 show the
Fig. 7 Geological sketch maps of 500-m level (A) and 450-m level (B) of the Shinyama 4D orebody. Numbers with capital are sample numbers.

REE patterns for clinopyroxene and garnet, being main constituents of the skarns. The clinopyroxenes exhibit moderate LREE enriched - HREE depleted patterns and negative Eu anomalies, and their REE contents decrease from the skarn I, II to III. The magnitude of negative Eu anomalies in the clinopyroxenes increases from the skarn I to III. The REE patterns of all garnets are characterized by the LREE depletion and MREE and HREE enrichment. The garnets in the skarn II exhibit slight MREE enrichment and small positive Eu anomalies, but those in the skarn III have large negative Eu anomalies. This difference of Eu behavior in garnets from the skarn II and the skarn III is the most conspicuous feature recognized in the Nippo zoned skarn. Comparing the REE patterns of clinopyroxene and garnet with those of whole rocks in the skarn II and III, it becomes clear that the clinopyroxene is a main host mineral for LREE and the garnet for MREE and HREE. Clinopyroxenes in igneous rocks are generally very poor in LREE, but clinopyroxene and garnet in eclogite contain high LREE and HREE, respectively (HASKIN, 1984), as in the skarns from the Nippo ore deposit.

**Zonation and REE Patterns of the Skarns in the Shinyama Ore Deposit**

A schematic geologic section along west-east cross section of the Shinyama 4D orebody is shown in Fig. 6. The skarn is formed along the boundary between limestone and diorite porphyry, and the copper deposit is embedded at the limestone side and the iron deposit at the diorite porphyry side. The ore deposits are situated on the 400 - 600-m levels, and the distribution area of skarn enlarges from the lower 400-m level to the upper 600-m level. Geological sketch maps of 500-m level and 450-m level are presented in Fig. 7.

The skarn is zoned and can be divided principally into garnet skarn on the diorite porphyry side and green skarn (clinopyroxene and/or amphibole-rich skarn) on the limestone side. Between the garnet skarn and the green skarn on the 500-m level, there is a spherical garnet skarn, in which matrix of disjointed garnet skarns is filled up with the green skarn. Epidote skarn is locally distrib-
Fig. 8 Chondrite-normalized REE patterns of the zoned skarns at the 500-m level of the Shinyama deposit. The garnet skarns at the 500-m level have negative Eu anomalies.

Fig. 9 Chondrite-normalized REE patterns of the zoned skarns at the 450-m level of the Shinyama deposit. The garnet skarns at the 450-m level show MREE enrichment and positive Eu anomalies.

The mineral assemblage is as follows; diorite porphyry: amphibole + biotite + clinopyroxene + plagioclase ± quartz, epidote skarn: epidote ± clinopyroxene ± amphibole, garnet skarn: garnet + clinopyroxene ± epidote ± amphibole + calcite + quartz, green skarn: clinopyroxene ± garnet ± amphibole ± calcite ± quartz. The mineral paragenesis of the assemblage in each skarn varies systematically due to the variations of temperature and chemical potential of CO₂ (OCHIAI, 1977; UCHIDA and IIYAMA, 1982; UCHIDA, 1986). Judging from the occurrence and chemical compositions, the epidote skarn may have originated from the diorite porphyry and the green skarn from the limestone. The garnet skarn shows an intermediate chemical composition of the epidote skarn and the green skarn. The initial boundary between the diorite porphyry and the limestone may have been located within the garnet skarn.

Figures 8 and 9 present chondrite-normalized REE patterns of the zoned skarns. The garnet skarns at the 500-m level have negative Eu anomalies. Enrichment to rather flat. The garnet skarn exhibits almost flat patterns with the HREE contents comparable to those of the diorite porphyry. The epidote skarn has a small positive Eu anomaly, but the garnet skarn and the green skarn show large negative Eu anomalies (Fig. 8). The garnet skarn at the 450-m level, being characterized by MREE enrichment, exhibits sharp convex patterns with the peak at Eu (Fig. 9).

REE patterns of garnets from the garnet skarn are shown in Fig. 10. The contrast of REE patterns between the garnets from the 450-m level, having positive Eu anomalies, and those from the 500-m level, showing negative Eu anomalies, is apparent in the figure. The garnets with positive Eu anomalies are richer in LREE and MREE than those with negative Eu anomalies. The REE patterns of garnets with positive Eu anomalies are similar to those of host garnet skarn, indicating that the REE abundance of the garnet essentially determines that of the garnet skarn.

Figure 11 shows the REE patterns of garnets from the garnet skarn around the 2D orebody at the 450-m level. These garnets have negative Eu anomalies, though they were collected from the same level as the 4D orebody, garnets from which...
Fig. 10 Chondrite-normalized REE patterns of garnets from the garnet skarns around 4D orebody at the 500-m and 450-m levels of the Shinyama deposit. Note that garnets at the 500-m and 450-m levels have negative and positive Eu anomalies, respectively.

Eu Anomalies of Garnet and Clinopyroxene and their Geological Significance

REE patterns of the analysed ten garnets are presented in Fig. 12. As mentioned above, the garnets exhibit large variations in the extent of Eu anomalies. "Negative Eu anomaly" is apparently indicated by the discontinuous depletion of Eu relative to adjacent Sm and Gd. On the other hand, "positive Eu anomaly" is not represented by the peak of only Eu, but by the protrusion of Sm, Eu and Gd. Judging from this nature of Eu anomalies, it is clear the negative Eu anomaly is due to the behavior of Eu as divalent cations, and the positive Eu anomaly as trivalent cations such as Sm and Gd. The main factor that controls Eu$^{2+}$/Eu$^{3+}$ ratios in minerals is the oxygen fugacity ($f_{O_2}$) prevailing during mineral formation (HENDERSON, 1984). The other factors which may affect Eu$^{2+}$/Eu$^{3+}$ ratio in the garnet are chemical composition of garnet, coexisting minerals (especially plagioclase), temperature and pressure. The temperature and pressure may not have been the cause of the difference in Eu$^{2+}$/Eu$^{3+}$...
ratio, because the difference in the oxidation state of Eu relates to the difference in skarn type rather than that in skarn deposit. The independence of oxidation state of Eu from chemical compositions of garnets is supported from the fact that both the garnets with positive and negative Eu anomalies in the Shinyama ore deposit have similar chemical compositions of andradite moles of 50-56%, which were determined by wet chemical techniques. The presence of plagioclase with positive Eu anomaly in the Nippo skarn II was not a factor to produce the garnets with negative Eu anomalies, because the garnet from the skarn II shows rather positive Eu anomalies. On the other hand, the garnet from the skarn III that has not plagioclase exhibits negative Eu anomalies.

It is well known that the extent of negative Eu anomalies of clinopyroxenes in igneous rocks and meteorites increases with a decrease of $f_{O_2}$ (McKAY, 1989). If we suppose that the same relation between the extent of negative Eu anomalies and the $f_{O_2}$ can apply for the skarn, the increase of the magnitude of negative Eu anomalies in the clinopyroxenes from the skarn I to the skarn III, shown in Fig. 4, indicates a decrease of $f_{O_2}$ from the skarn I to the skarn III. The clinopyroxene and garnet in the skarn III are inferred to have formed under lower $f_{O_2}$ conditions. The mineral assemblages of the skarn I, skarn II and skarn III are different from each other, and the skarn I is devoid of garnet, but contains plagioclase as a main constituent. Plagioclase may augment the extent of negative Eu anomaly in the clinopyroxene from the skarn I, because plagioclase is commonly considered to have positive Eu anomaly. However, the magnitude of negative Eu anomaly in the clinopyroxene from the skarn I is small. This fact supports that the increase of the extent of negative Eu anomalies in the clinopyroxene from the skarn I to the skarn III was caused by the decrease of $f_{O_2}$.

Garnets in igneous and metamorphic rocks generally show negative Eu anomalies (IRVING and FREY, 1978; HICKMOTT and SHIMIZU, 1987). In skarnized chalk xenoliths in volcanic rocks in Isle of Arran, Scotland, the garnet (andradite) formed at an early stage exceptionally have positive Eu anomalies (CRESSEY, 1987). The author considered that trivalent Eu is preferentially taken into garnet relative to divalent Eu, and that higher $f_{O_2}$ at the early stage had induced the positive Eu anomaly of the early garnet. The garnets experimentally formed from a basaltic melt at high $f_{O_2}$ conditions, have flat REE patterns with no Eu anomaly (SHIMIZU and KUSHIRO, 1975).

Thus, the variation of Eu anomaly in garnet seems to depend mainly on the $f_{O_2}$. Then what is the main factor which controls the variation of $f_{O_2}$? The factor may be the space relation between the quartz diorite-diorite porphyry and the limestone. In the Nippo ore deposit, garnets with negative Eu anomalies are found in the skarn III situated at the limestone side, whereas garnets with positive Eu anomalies occur in the skarn II at the quartz diorite side. YUI (1966) pointed out that graphite in limestone plays an important role in lowering $f_{O_2}$ during skarnization. Graphite in limestone may have caused a decline of $f_{O_2}$ and consequently negative Eu anomalies of the garnets in the skarn III. The same idea can be applied for the Shinyama ore deposit, and the garnets with negative Eu anomalies is considered to have derived from graphite-bearing limestone. Graphite has not been found in the crystalline limestone of the present study. The Nagaiwa-Onimaru unmetamorphosed limestone which is the same strata as the crystalline limestone of the Kamaishi district, however, is impure and contains carbonaceous materials (TAKEDA and YOSHIDA, 1962).

Garnets with positive Eu anomalies need further explanation. One possibility is that the dioritic rocks are the cause of high $f_{O_2}$ that produced the positive Eu anomalies of the garnets. However, the garnets with positive Eu anomalies have been never reported from igneous rocks. Another possibility is that the $f_{O_2}$ in hydrothermal fluids was initially high. In the Shinyama ore deposit, the garnet skarn at the 450-m level, the garnets from which show positive Eu anomalies (Fig. 10), is narrow in width and intimately accompanied by magnetite orebody. On the other hand, the garnet skarn at the 500-m level, the garnets from which have negative Eu anomalies, is broad in width (Fig. 7). The width of zoned skarn in the Nippo ore deposit is intermediate between the zoned skarn at the 450-m level and that at the 500-m level in the Shinyama ore deposit. The wider in width of zoned skarn, the larger the amount of metasomatic reaction between hydrothermal
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During the metasomatic reaction, the $f_{O_2}$ in hydrothermal fluids was declined because of reaction with graphite-bearing limestone. It can be considered that initial hydrothermal fluids with higher $f_{O_2}$ reacted with dioritic rocks to form the endomorphic garnet skarn with positive Eu anomalies. The garnet skarn with negative Eu anomalies was formed by the reaction between limestone and the initial fluids, or between dioritic rocks and the secondary fluids with lower $f_{O_2}$. The secondary lower $f_{O_2}$ fluid were originated by the reaction of the initial fluids with limestone. Since the mineral paragenesis of garnet + clinopyroxene + magnetite + quartz is recognized in the garnet skarn from the Shinyama ore deposit, it can be estimated that the initial $f_{O_2}$ of hydrothermal fluids was higher than the stability field of graphite (approximately Ni-NiO oxygen buffer) (LIOU, 1984), and that the $f_{O_2}$ was decreased to the QFM oxygen buffer at 1 kb and 500°C owing to the reaction of the fluids with graphite-bearing limestone.

Conclusions

The REE patterns of garnet skarn and garnet from the Nippo and Shinyama ore deposits in the Kamaishi mine are presented. The garnet skarn and garnet show large variations of Eu anomalies from positive to negative. The initial hydrothermal fluids with higher $f_{O_2}$ had decreased $f_{O_2}$ because of their metasomatic reaction with graphite-bearing limestone. The garnets with positive Eu anomalies were formed by the reaction of dioritic rocks with the initial hydrothermal fluids with higher $f_{O_2}$. The garnets with negative Eu anomalies were produced by the reaction between limestone and the initial fluids, or between dioritic rocks and the secondary lower $f_{O_2}$ fluids which had been affected by limestone.

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References


釜石鉱山のスカルンの生成過程における希土類元素の挙動

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要旨：釜石鉱山の日峰鉱床と新山鉱床におけるスカルン帯のスカルン、およびザクロ石と単斜輝石について、コンドライトで規格した希土類元素(REE)パターンを示し、スカルン帯の生成過程でのREEの挙動を解析した。スカルン帯は関連岩類と石灰岩との間に発達し、全岩のREEは関連岩側から石灰岩へと減少する。スカルンのREEは関連岩類に由来し、熱水溶液からの供給はほとんどなかったものと考えられる。単斜輝石は負のEu異常を示し、その大きさは関連岩側から石灰岩へと増大する。ザクロ石のEu異常は正または負と大きく変動する。鉱物のEu²⁺/Eu³⁺比を決める主な要因は酸素フーガティー（fo₂）であり、単斜輝石の負のEu異常はfo₂の減少と共に大きくなり、ザクロ石はEu³⁺をEu²⁺よりも優先的に取り込む。熱水溶液のfo₂は石墨を含む石灰岩との交代反応により次第に減少した。ザクロ石のEu異常の大きな変化は、高いfo₂をもった初生の熱水溶液と低いfo₂の石灰岩との反応によって生じたfo₂の変動の反映である。