PHASE RELATIONS IN THE Fe–Ni–S SYSTEM FROM 875 TO 650 °C

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ABSTRACT

High-form pentlandite of composition Fe\textsubscript{4.93}Ni\textsubscript{4.06}S\textsubscript{8.01} first crystallizes by peritectic reaction between liquid and monosulfide solid-solution at 870 ± 3 °C (865 ± 3 °C for high-form pentlandite with Fe=Ni in at.% in the Fe–Ni–S system; it forms a limited solid-solution from Fe\textsubscript{5.06}Ni\textsubscript{3.98}S\textsubscript{7.99} to Fe\textsubscript{3.81}Ni\textsubscript{5.24}S\textsubscript{7.96} including the ideal composition Fe\textsubscript{4.50}Ni\textsubscript{4.50}S\textsubscript{8.00} at 850 °C. The solid solution grows rapidly to extend its field toward the Ni-rich side with decreasing temperature and connects with β\textsubscript{1} (44.7 at.% S) in the Ni–S join at 806 ± 3 °C (peritectic between liquid and Ni\textsubscript{1–x}S). Below the peritectic temperature, high-form pentlandite (metal-rich composition) crystallizes directly from liquid. This crystallization continues to the eutectic (746 ± 3 °C for the high form with Fe=Ni) with decreasing temperature, and the high-form solid solution grows still more. Crystallization of the monosulfide solid-solution and high-form pentlandite solid solution from liquid finishes at 762 ± 3 °C and 739 ± 3 °C, respectively. The high-form pentlandite solid solution extended from the Ni–S join is maintained at 700 and 650 °C and coexists with monosulfide solid-solution and/or with liquid (870 to 739 °C), and/or with β\textsubscript{1} or its solid solution (800 to 503 °C), and/or with γ (762 to 579 °C).

In geological processes such as the formation of Ni-Cu ore deposits, pentlandite can crystallize as the high form from liquid (sulfide magma) by peritectic and eutectic reactions at comparatively high temperatures from 870 to 739 °C (Fe–Ni–S system). Pentlandite is also produced by the breakdown of the high form at the pseudoeutectoid (or ternary eutectoid). Pentlandite can further be formed by exsolution from monosulfide solid-solution below 600 °C, and from the ternary β\textsubscript{1} phase.

Keywords: Fe–Ni–S system, high-form pentlandite, pentlandite, monosulfide solid-solution, β\textsubscript{1} solid-solution.

INTRODUCTION

This paper continues from our previous paper (Kitakaze et al. 2011) on the Fe–Ni–S system from 650 to 450 °C; results regarding phase relations from 875 to 650 °C are the main topic. Since the study by Kullerud (1962, 1963a), it has been assumed that pentlandite (Fe\textsubscript{4.5}Ni\textsubscript{4.5}S\textsubscript{8.0}) is present as a stable phase below 610 ± 3 °C and breaks down to a mixture of Ni\textsubscript{3+}S\textsubscript{2} and pyrrhotite (monosulfide solid-solution) at or above this temperature (Kullerud et al. 1969, Craig & Scott 1976, Kosyakov & Sinyakova 2006). However, Sugaki et al. (1983, 1984) and Kitakaze et al. (2011) found that pentlandite (Fe=Ni in at.%) does not break down at this temperature, but transforms into a higher form, which is stable up to 865 ± 3 °C. The high-form pentlandite is unquenchable and always shows the X-ray pattern for pentlandite (low form) at room temperature. Sugaki & Kitakaze (1992, 1998) and Kitakaze et al. (2011) verified using high-temperature X-ray diffraction that the high form (Fe\textsubscript{4.50}Ni\textsubscript{4.50}S\textsubscript{7.80}) has a primitive cubic cell with a = 5.189 Å (620 °C), corresponding to one-half of the cell edge of pentlandite. The high-low inversion is reversible, and might be an order-disorder (perhaps defect sphalerite structure) transformation.

Sugaki et al. (1983, 1984) also found that high-form pentlandite appears as an extensive solid solution from a more Fe-rich composition than Fe\textsubscript{4.5}Ni\textsubscript{4.5}S\textsubscript{8.0} to Ni\textsubscript{3+}S\textsubscript{2} on the Ni–S boundary of the Fe–Ni–S system at 800 and 650 °C. Hayashi (1985) recognized the existence of the same solid solution in the quaternary...
Cu–Fe–Ni–S at 850 and 650 °C. Fedorova & Sinyakova (1993) and Karup-Moller & Makovicky (1995) reported an extended heazlewoodite solid-solution \((\text{Fe},\text{Ni})_3\text{S}_2\) at 820 and 600 °C and an elongated \((\text{Ni},\text{Fe})_3\text{S}_2\) solid-solution at 725 °C, respectively, using the terminology of the authors. Both phases correspond to the high-form pentlandite – \(\text{Ni}_3\text{S}_2\) solid-solution of Sugaki et al. (1983, 1984) and Kitakaze et al. (2011).

On the other hand, Lin et al. (1978), Sharma & Change (1980), Singleton et al. (1991), and Kitakaze & Sugaki (2001) found that \(\text{Ni}_3\text{S}_2\) \((\beta)\) in binary Ni–S is not a monophase, but consists of two limited solid-solutions of phases \(\beta_1\) (\(\text{Ni}_3\text{S}_2\), corresponding to high-form heazlewoodite) and \(\beta_2\) (\(\text{Ni}_4\text{S}_3\), a high-temperature phase) with a narrow immiscibility field between them, over the temperature range from 524 to 806 °C, using a gas equilibration technique. Sugaki & Kitakaze (1996), Kitakaze & Sugaki (2001), and Kitakaze et al. (2011) ascertained crystallographically the existence of phases \(\beta_1\) and \(\beta_2\) in the \(\text{Ni}_{1-2}\text{S}_2\) field using high-temperature X-ray diffraction techniques.

The appearance of high-form pentlandite \(\beta_1\) solid-solution and \(\beta_2\) as stable phases required the reexamination and revision of the phase diagrams of the system Fe–Ni–S above 650 °C as shown by previous authors (Kullerud 1963b, Kullerud et al. 1969, Hsieh et al. 1982, Baker 1983, Hayashi 1985, Fedorova & Sinyakova 1993, Karup-Moller & Makovicky 1995, Peregoedova & Ohnensetter 2002). Thus, we investigated the isotherms at temperatures from 875 to 650 °C. In this paper, we present new experimental data in the Fe–Ni–S system, especially phase relations with high- and low-form pentlandites, \(\beta_1\) and \(\beta_2\), above 650 °C and their thermal stabilities.

Chemical compositions and crystal data for minerals and solid phases appearing in this study and produced in the Fe–Ni–S system above 650 °C are given in Table 1.

**Experimental Procedure**

*Synthesis and equilibrium experiments*

The syntheses were carried out by the evacuated silica-glass tube method. The starting materials, Fe (99.999%) and Ni (99.999%) from Johnson Matthey Co. Ltd. and S (99.99%) from Kanto Chemical Co. Ltd., were weighed for the desired composition of each experiment, and then sealed in transparent silica-glass tubes under a vacuum of \(1.33 \times 10^{-4}\) Pa (\(10^{-3}\) torr).

The sealed tubes with their charges were kept at 850, 800, 750, 700, and 650 °C for 10 days. The products were ground and mixed under acetone in an evacuated silica tube and reheated at 850, 800, 750, 700, and 650 °C for at least 3, 5, 15, 30, and 40 days, respectively. After reheating, the tubes were rapidly cooled in ice water. The final products were aggregates of fine anhedral grains, 20 to 100 µm in size, except for S and sulfide liquids.

**Microscopic examination**

All the experimental products were examined with a reflected light microscope. Among the products, pyrite, vaesite, monosulfide solid-solution, and metals of \(\alpha\) ("kamacite" = iron) and \(\gamma\) (tamite) compositions were the homogeneous phases after quenching. However, high-form pentlandite-\(\beta_1\) solid solution, \(\beta_2\), and sulfide liquid were not present as mono-phases after quenching, and the products consisted of cooling products that appeared as consequences of phase transformation, eutectic, eutectoid, peritectic, peritectoid, or exsolution reactions. Because the experimental products composed of low-form pentlandite, godlevskite, heazlewoodite, monosulfide solid-solution, and metal phases have small grain sizes, backscattered electron (BSE) images, obtained with an electron-probe microanalyzer (EPMA), were generally used in addition to examination with a reflected light microscope.

**X-ray powder diffraction**

Because high-form pentlandite-\(\beta_1\) solid-solution and the \(\beta_2\) phase are unquenchable, X-ray powder diffractometers (JEOL JDX-7S and Rigaku Geigerflex RAD-C) with high-temperature heating units (JEOL DX-GOH V2 and Rigaku CN2311B1) were used for identification of these phases using the method described by Kitakaze et al. (2011).

**Electron probe microanalysis**

The chemical compositions of the phases produced were obtained by EPMA (JEOL JXA 8800, WD mode by ZAF correction, beam diameter less than 10 µm) with analytical conditions as follows: accelerating voltage 20 kV; specimen current 0.010 µA; curved crystal LiF for FeK\(\alpha\) and NiK\(\alpha\), and TAP for SK\(\alpha\). Synthetic FeS and NiS as were used as standards for Fe and S, and for Ni, respectively, in sulfides, and pure Fe and Ni metals were used as standards for Fe and Ni, respectively, in the metal phases.

Nickel-rich high-form pentlandite and \(\beta_2\) have similar compositions and are accompanied by cooling products such as low pentlandite, monosulfide solid-solution, godlevskite, heazlewoodite, and metal phases. The phase assemblages were confirmed by high-temperature X-ray diffraction for each temperature. In reference to these results, bulk compositions were obtained by analysis with a larger beam diameter (20–40 µm) and by averaging values for 10 to 15 point analysis.
phase diagram. These phase changes, such as liquidus, peritectic, eutectic, obtain the temperatures of the reactions causing the

Differential thermal analysis (DTA) for metals and liquid.

The chemical formulae Fe$_x$Ni$_y$S$_z$ of sulfide and liquid phases in this paper indicate the atomic values converted from the electron probe microanalysis data as follows: $z = 2.00$ for vaesite and pyrite; $z = 1.00$ for monosulfide solid-solution; $x + y + z = 17.00$ for high-form pentlandite and pentlandite; and $x + y + z = 1.00$ for metals and liquid.

Differential thermal analysis (DTA)

Differential thermal analysis using the evacuated silica-glass tube as a reaction vessel was performed to obtain the temperatures of the reactions causing the phase changes, such as liquidus, peritectic, eutectic, and phase transitions in the phase diagram. These procedures were approximately the same as those described by Kitakaze et al. (2011).

Experimental Results

Phase relations at 875 °C

Phase relations in the Fe–Ni–S system at 875 °C were obtained from the equilibrium experimental data and the EPMA data for the synthetic products, and are shown in Figure 1. Only six phases appeared at this temperature: four solid phases, e.g., vaesite, monosulfide solid-solution, $\alpha$, and $\gamma$, and two liquid phases, e.g., sulfide and sulfur. Monosulfide solid solution appears as the first sulfide phase, Fe$_{1}$–S (Fe$_{0.93}$S$_{1.00}$), in the system at 1188 °C (Rau 1975, Kusbaschewski 1982, Okamoto 1990), extends its field successively in the NiS direction with decreasing temperature, and forms a complete solid solution between Fe$_{1}$–S (1C) and Ni$_{1}$–S below 999 ± 3 °C, at which temperature Ni$_{1}$–S melts congruently (Kullerud & Yund 1962, Arnold & Malik 1975, Rau 1975, Lin et al. 1978, Sharma & Chang 1980, Singleton et al. 1991). Vaesite, which crystallized as the stable phase NiS$_{2}$ via a synthetic reaction between two immiscible liquids, Ni-rich liquid and sulfur liquid, at 1022 ± 3 °C (Arnold & Malik 1975, Lin et al. 1978, Sharma & Chang 1980, Singleton et al. 1991), has a limited solid-solution ranging from Ni$_{2}$ to Fe$_{0.18}$Ni$_{0.82}$S$_{2.00}$ along the FeS$_{2}$–Ni$_{2}$S$_{2}$ join at 875 °C. The sulfide liquid phase occupies a wide field extending from the Ni–S join toward the inside of the ternary up to Fe$_{0.43}$Ni$_{0.17}$S$_{0.41}$.

In the figure, three univariant assembles are found, as follows: (1) vaesite (Fe$_{0.13}$Ni$_{0.86}$S$_{2.00}$) + monosulfide solid-solution (Fe$_{0.23}$Ni$_{0.58}$S$_{1.00}$) + S (liquid); (2) monosulfide (Fe$_{0.89}$Ni$_{0.11}$S$_{1.00}$) + liquid (Fe$_{0.40}$Ni$_{0.60}$S$_{0.41}$) + $\gamma$ (Fe$_{0.54}$Ni$_{0.46}$), and (3) monosulfide solid-solution (Fe$_{0.94}$Ni$_{0.06}$S$_{1.00}$) + $\alpha$ (Fe$_{0.90}$Ni$_{0.01}$) + $\gamma$(Fe$_{0.97}$Ni$_{0.03}$).

### Table 1. Chemical Compositions and Crystallographic Data for Minerals and Phases Appearing in This Study

<table>
<thead>
<tr>
<th>Minerals and phases</th>
<th>Symbols</th>
<th>Compositions</th>
<th>Structure types</th>
<th>Cell edges in Å</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrite</td>
<td>py</td>
<td>(Fe,Ni)$_2$S</td>
<td>Cubic $Pa\bar{3}$</td>
<td>a 5.3825</td>
<td>Fujii et al. (1986)</td>
</tr>
<tr>
<td>Vaesite</td>
<td>vs</td>
<td>(Ni,Fe)$_2$S</td>
<td>Cubic $Pa\bar{3}$</td>
<td>a 5.6765</td>
<td>Nowack et al. (1991)</td>
</tr>
<tr>
<td>Monosulfide solid-solution</td>
<td>mss</td>
<td>(Fe,Ni)$_{1-x}$S</td>
<td>Hexagonal $P\bar{6}_3/mmc$</td>
<td>a 3.45, c 5.6</td>
<td>Craig &amp; Scott (1976)</td>
</tr>
<tr>
<td>High-form pentlandite</td>
<td>hpn</td>
<td>(Fe,Ni)$_3$S$_8$</td>
<td>Cubic $Pn\bar{3}m$</td>
<td>a 5.245(650 °C)</td>
<td>Sugaki &amp; Kitakaze (1998)</td>
</tr>
<tr>
<td>Pentlandite</td>
<td>pn</td>
<td>(Fe,Ni)$_6$S$_8$</td>
<td>Cubic $Fm\bar{3}m$</td>
<td>a 10.100</td>
<td>Rajamani &amp; Prewitt (1973)</td>
</tr>
<tr>
<td>Phase $\beta_2$</td>
<td>$\beta_2$</td>
<td>Ni$_6$S$_3$(SS)</td>
<td>Cubic $Pn\bar{3}m$</td>
<td>a 5.140(600 °C)</td>
<td>Sugaki &amp; Kitakaze (1998)</td>
</tr>
<tr>
<td>Phase $\beta_1$</td>
<td>$\beta_1$</td>
<td>Ni$_5$S$_2$(SS)</td>
<td>Cubic $Fm\bar{3}m$</td>
<td>a 5.210(600 °C)</td>
<td>Kitakaze &amp; Sugaki (2001)</td>
</tr>
<tr>
<td>Phase $\alpha$ (&quot;kamagate&quot;)</td>
<td>$\alpha$</td>
<td>(Fe,Ni)</td>
<td>Cubic $Fm\bar{3}m$</td>
<td>a 2.860</td>
<td>Ramsden &amp; Cameron (1966)</td>
</tr>
<tr>
<td>Phase $\gamma$ (taenite)</td>
<td>$\gamma$</td>
<td>Fe$<em>{0.96}$Ni$</em>{0.04}$</td>
<td>Cubic $Fm\bar{3}m$</td>
<td>a 3.587</td>
<td>Dumpich et al. (1987)</td>
</tr>
</tbody>
</table>

Note: SS = solid-solution.

Standard deviation of the analytical values obtained by EPMA were as follows: (1) ±0.1 wt.% for Fe, Ni, and S of a monophase without quench products, such as pyrite, vaesite, pentlandite, and monosulfide solid-solution; (2) ±0.3 wt.% for Fe, Ni, and S in the phases with quenching products, such as high-form pentlandite solid solution, $\beta_2$, and liquid.

The chemical formulae Fe$_x$Ni$_y$S$_z$ of sulfide and liquid phases in this paper indicate the atomic values converted from the electron probe microanalysis data as follows: $z = 2.00$ for vaesite and pyrite; $z = 1.00$ for monosulfide solid-solution; $x + y + z = 17.00$ for high-form pentlandite and pentlandite; and $x + y + z = 1.00$ for metals and liquid.
Phase relations from 875 to 850 °C

High-form pentlandite with (Fe\(4.93\)Ni\(4.06\)S\(8.01\)) first appears as a stable phase at 870 ± 3 °C as a result of a pseudoperitectic reaction between monosulfide solid solution (Fe\(0.89\)Ni\(0.11\)S\(1.00\)) and liquid (Fe\(0.43\)Ni\(0.17\)S\(0.41\)). This reaction is reversible and was documented by high-temperature X-ray diffraction, DTA, EPMA, and microscopic examinations. It proceeds toward the more Ni-rich or S-rich portion (or both) of the solid solution with decreasing temperature.

Phase relations at 850 °C

The phase relations based on the data from the equilibrium experiments and the EPMA at 850 °C are shown in Figure 2. The stable phases, such as S(l), vaesite, monosulfide solid solution, high-form pentlandite, sulfide liquid, \(\alpha\), and \(\gamma\), are shown in the Figure. At 850 °C, high-form pentlandite appears with a limited solid-solution from Fe\(5.08\)Ni\(3.93\)S\(7.99\) to Fe\(3.81\)Ni\(5.24\)S\(7.96\) including Fe\(4.50\)Ni\(5.50\)S\(8.00\). The liquid phase occupies a wide field extending from the Ni–S

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**Fig. 1.** The phase diagram in the Fe–Ni–S system at 875 °C in the presence of an equilibrium vapor. Abbreviations: See Table 1; liq = liquid, S(l) = sulfur liquid.

**Fig. 2.** The phase diagram in the Fe–Ni–S system at 850 °C in the presence of an equilibrium vapor. Abbreviations: See Table 1; liq = liquid, S(l) = sulfur liquid.
The phase relations at 800 °C were obtained from the equilibrium experiment and the EPMA data and are shown in Figure 3. The field for the high-form pentlandite solid solution extends rapidly toward the Ni-rich side with decreasing temperature below 850 °C, and reaches the Fe-free \( \beta_2 \) (44.7 at.% S) point in the Ni–S join at 806 ± 3 °C, at which temperature \( \beta_2 \) crystallizes (Lin et al. 1978). As seen in the Figure, a continuous solid solution from high-form pentlandite to \( \beta_2 \) exists at 800 °C. The Fe-rich end composition of the solid solution (\( \sim 5.29 \text{Ni}_{3.74} \text{S}_{7.97} \)) at 800 °C contains slightly more Fe than that at 850 °C. Phase \( \beta_1 \) with the S-richest composition (\( \sim 42.9 \) at.% S) appears by peritectic reaction between \( \beta_2 \) and liquid in the Ni–S join at 800 °C. The liquid phase still occupies an extensive field, but it retreats toward the Ni–S join at 800 °C. The continuous monosulfide solid solution is present as at 850 °C, but it cannot coexist with the liquid phase, except the Fe-rich portion, because of the intervening continuous solid solution of high-form pentlandite–\( \beta_2 \) at 800 °C. The high-form pentlandite–\( \beta_2 \) solid solution (hereafter referred to as high-form pentlandite solid solution) coexists with the monosulfide solid solution and/or liquid. However, it cannot yet coexist with \( \gamma \) due to the existence of the intervening liquid field. The monosulfide solid solution near FeS coexists with \( \alpha \) and Fe-rich \( \gamma \), while the metal-rich liquid coexists with Ni-rich \( \gamma \).

Five univariant assemblages are found in the isotherm at 800 °C as follows: (1) high-form pentlandite solid solution coexists with monosulfide solid solution and/or liquid. The \( \alpha \) (Fe\(_{0.99}\)Ni\(_{0.01}\)) phase coexists with \( \gamma \) (Fe\(_{0.98}\)Ni\(_{0.02}\)) (Kubaschewski 1982, Swartzendruber et al. 1993) and monosulfide solid-solution. Two univariant assemblages were found as follows: (1) high-form pentlandite (Fe\(_{5.08}\)Ni\(_{3.93}\)S\(_{7.99}\)) + monosulfide solid-solution (Fe\(_{0.87}\)Ni\(_{0.12}\)S\(_{1.00}\)) + c\(_{(\text{Fe}_{0.51}\text{Ni}_{0.49})}\); and (2) high-form pentlandite (Fe\(_{3.81}\)Ni\(_{5.24}\)S\(_{7.96}\)) + monosulfide solid-solution (Fe\(_{0.44}\)Ni\(_{0.53}\)S\(_{1.00}\)) + liquid (Fe\(_{0.39}\)Ni\(_{0.2} \text{S}_{0.40}\)) in the metal-rich portion. The high-form pentlandite solid solution can’t coexist with \( \gamma \) because of the existence of an extensive liquid field. The liquid (Fe\(_{0.40}\)Ni\(_{0.22}\)S\(_{0.38}\)) on the metal-rich side coexists with monosulfide solid solution (Fe\(_{0.95}\)Ni\(_{0.04}\)S\(_{1.00}\)) and \( \gamma \) (Fe\(_{0.52}\)Ni\(_{0.48}\)) as a univariant assemblage. Most Fe-rich monosulfide solid solution (\( \sim \)FeS) can coexist with \( \alpha \) (Fe\(_{0.99}\)Ni\(_{0.01}\)) and \( \gamma \) (Fe\(_{0.98}\)Ni\(_{0.02}\)) as a univariant assemblage.

In the S-rich portion of the system, vaesite (Fe\(_{0.23}\)Ni\(_{0.76}\)S\(_{2.00}\)) coexists with monosulfide solid solution (Fe\(_{0.53}\)Ni\(_{0.27}\)S\(_{1.00}\)) and S(liq) as a univariant assemblage. No pyrite occurs at this temperature.

The phase relations of the metal-rich portions at 850 °C are similar to those noted at 820 °C by Fedorova & Sinyakova (1993). However, the field for high-form pentlandite solid solution is more S-rich than that of the heazlewoodite solid solution. The Fe-rich ends of the high-form pentlandite and liquid are more Fe-rich by then.
pentlandite (Fe_{5.29}Ni_{3.74}S_{7.97}) + monosulfide solid solution (Fe_{0.87}Ni_{0.13}S_{1.00}) + liquid (Fe_{0.31}Ni_{0.26}S_{0.41}); (2) monosulfide solid solution (Fe_{0.94}Ni_{0.04}S_{1.00}) + liquid (Fe_{0.30}Ni_{0.33}S_{0.38}) + c(Fe_{0.48}Ni_{0.52}); (3) monosulfide solid solution (Fe_{0.99}Ni_{0.01}S_{1.00}) + a(Fe_{0.98}Ni_{0.02}) + c(Fe_{0.90}Ni_{0.04}) (Kubaschewski 1982); (4) b_{1} (Fe_{0.55}Ni_{2.34}S_{2.00}) + liquid (Fe_{0.14}Ni_{0.50}S_{0.37}); (5) monosulfide solid solution (Fe_{0.72}Ni_{0.10}S_{1.00}) + vaesite (Fe_{0.59}Ni_{0.41}S_{2.00}) + S(liquid).

**Phase relations from 800 to 750 °C**

On cooling from 800 °C, the liquid phase retreats further toward the Ni-rich side. The tie-lines between monosulfide solid solution and liquid are replaced by those between high-form pentlandite and γ at 762 ± 3 °C (invariant). This tie-line change was ascertained by DTA, microscopic examination, and EPMA data. The reaction is reversible.

Below 762 ± 3 °C monosulfide solid solution cannot crystallize from liquid via a pseudoeutectic reaction. Phase β_{1} grows and quickly extends as a solid solution from the Ni–S join within the ternary field with decreasing temperature, forming a solid solution with a fairly large area.

**Phase relation at 750 °C**

The phase relation determined from the data for equilibrium studies and EPMA at 750 °C is shown in Figure 4. There are five univariant assemblages in the system as follows: (1) monosulfide solid solution (Fe_{0.86}Ni_{0.13}S_{1.00}) + high-form pentlandite (Fe_{5.44}Ni_{3.60}S_{7.96}) + γ(Fe_{0.42}Ni_{0.56}); (2) high-form pentlandite (Fe_{4.20}Ni_{5.32}S_{7.48}) + liquid (Fe_{0.20}Ni_{0.44}S_{0.36}) + γ(Fe_{0.34}Ni_{0.66}); (3) high-form pentlandite (Fe_{2.35}Ni_{7.21}S_{2.45}) + β_{1}(Fe_{0.53}Ni_{2.44}S_{2.00}) + liquid (Fe_{0.14}Ni_{0.50}S_{0.37}); (4) monosulfide solid solution (Fe_{0.97}Ni_{0.03}S_{1.00}) + α(Fe_{0.95}Ni_{0.05}) + γ(Fe_{0.90}Ni_{0.10}); (5) monosulfide solid solution (Fe_{0.72}Ni_{0.10}S_{1.00}) + vaesite (Fe_{0.59}Ni_{0.41}S_{2.00}) + S(liquid).

**Relation from 750 to 700 °C**

Pyrite appears in the system at 743 °C with vaesite and monosulfide solid solution.

Other tie-line changes from high-form pentlandite and liquid to α and γ at 739 ± 3 °C were ascertained by DTA, microscopic examination, and EPMA. The compositions of the four coexisting phases were estimated to be Fe_{3.03}Ni_{6.41}S_{7.57} for high-form pentlandite, Fe_{0.78}Ni_{2.10}S_{2.00} for β_{1}, Fe_{0.17}Ni_{0.48}S_{0.35} for liquid, and Fe_{0.25}Ni_{0.75} for γ as the invariant association. Below this temperature, no crystallization of high-form pentlandite from liquid as pseudoeutectic is found.

**Phase relations at 700 °C**

The isothermal phase diagram at 700 °C, obtained from the equilibrium experimental and EPMA data for the phases produced, is shown in Figure 5. High-form pentlandite continues as an elongated solid-solution from Fe_{5.07}Ni_{4.03}S_{7.90} to phase β_{2} in the Ni–S join (~43.0–44.5 at.% S). The liquid field shrinks toward the Ni-rich side, but persists as a small field reaching...
the Ni–S join. The Fe-rich portion of the metal-rich side of the high-form pentlandite solid solution coexists with γ, whereas its Ni-rich portion coexists with β₁ solid solution. On the other hand, metal-rich β₁ solid solution coexists with S-rich liquid, whereas metal-rich liquid coexists with Ni-rich γ. Monosulfide solid solution cannot coexist with β₁ solid solution because the tie-lines between the high-form pentlandite solid solution and γ are more stable. Except for the most Fe-rich portion, the phase β₁ solid solution cannot yet coexist with γ because of the intervening liquid phase.

Four univariant assemblages are found in the metal-rich portion of the system as follows: (1) monosulfide solid solution (Fe_{0.98}Ni_{0.01}S_{1.00}) + α (Fe_{0.96}Ni_{0.04}) + γ (Fe_{0.90}Ni_{0.10}) (Kubaschewski 1982, Swartzendruber et al. 1993); (2) high-form pentlandite (Fe_{5.07}Ni_{4.05}S_{7.90}) + monosulfide solid solution (Fe_{0.93} Ni_{0.05}S_{1.00}) + γ (Fe_{0.40}Ni_{0.60}); (3) high-form pentlandite (Fe_{5.33}Ni_{6.40}S_{7.48}) + β₁ (Fe_{0.71}Ni_{2.12}S_{2.00}) + γ (Fe_{0.28}Ni_{0.75}); (4) β₁ (Fe_{0.67}Ni_{2.32}S_{2.00}) + liquid (Fe_{0.12}Ni_{0.53}S_{0.35}) + γ (Fe_{0.21}Ni_{0.79}).

In the S-rich portion of the system, pyrite appears at 742 ± 1 °C (Kullerud & Yoder 1959, Barton & Skinner 1979, Kubaschewski 1982) on the Fe–S join and forms a limited solid solution from FeS₂ to Fe_{0.89}Ni_{0.11}S_{2.00} at 700 °C. Vaesite also has a limited solid solution from NiS₂ to Fe_{0.29}Ni_{0.71}S_{2.00}. Both disulfides coexist separately with S (liquid) or monosulfide solid solution. The Ni-rich end of the pyrite and Fe-rich end of the vaesite solid solution coexist and form two univariant assemblages with monosulfide solid solution (Fe_{0.74}Ni_{0.09}S_{1.00}) or S (liquid).

Karup-Møller & Makovicky (1995) showed an isothermal phase diagram °C in the Fe–Ni–S system at 725 °C. Their phase relations are similar to those at 700 °C in this study. However, because phase β₁ and β₂ were not differentiated by them, the phase relations differ from those of the present study.

**Phase relations at 650 °C**

The isothermal phase diagram at 650 °C is shown in Figure 6. The high-form pentlandite solid solution field is slightly longer and wider (Sugaki & Kitakaze 1996, Kitakaze et al. 2011). The monosulfide solid solution still exists and retains the complete solid solution. The field for phase β₁ contracts to become smaller than at 700 °C. The liquid field reduces its area remarkably with decreasing temperature, but still retains a very small field slightly jutting out from the Ni–S join. The metal-rich side of the high-form pentlandite solid solution, except the Ni-rich portion, coexists with γ as at 700 °C. Phase β₁, except for its Ni-rich portion, can coexist with γ due to the retreat of the liquid field.

In the metal-rich portion, four univariant assemblages are found as follows: (1) monosulfide solid solution (Fe_{0.98}Ni_{0.01}S_{1.00}) + α (Fe_{0.95}Ni_{0.05}) + γ (Fe_{0.90}Ni_{0.10}) (Kubaschewski 1982, Swartzendruber et al. 1993); (2) high-form pentlandite (Fe_{5.41}Ni_{3.65}S_{7.94}) + monosulfide solid solution (Fe_{0.89} Ni_{0.07}S_{1.00}) + γ (Fe_{0.36}Ni_{0.64}); (3) high-form pentlandite (Fe_{2.89}Ni_{6.73}S_{7.36}) + β₁ (Fe_{0.56}Ni_{2.33}S_{2.00}) + γ

fig. 5. The isothermal diagram in the Fe–Ni–S system at 700 °C in the presence of an equilibrium vapor. Abbreviations: See Table 1.
Phase relations along the Fe_{4.5}Ni_{4.5}–S and Fe_{0.9}S–Ni_{3}S_{2} joins in the Fe–Ni–S system

The phase relations were investigated along the pseudobinary Fe_{4.5}Ni_{4.5}–S join at temperatures from 1000 to 450 °C, with a particular focus on a limited compositional range from 35 to 53 at.%, in order to unravel the thermal stability range of high- and low-form pentlandite coexisting with monosulfide solid solution and γ (Fig. 7). A similar diagram was previously reported by Sugaki & Kitakaze (1998), but there were some minor mistakes of phase assemblages for pseudoeutectoid, pseudoeutectic, and pseudoperitectoid in consideration as ternary phase relations.

The low-form pentlandite with Fe_{4.5}Ni_{4.5}S_{7.95} inverts to high-form at 615 °C on this join. The relations between low-form and high-form were described in detail in our previous paper (Kitakaze et al. 2011). The high-form solid solution with coexisting monosulfide solid solution is stable up to about 860 °C. However, high-form pentlandite on the metal-rich side is stable up to 750 °C, and has a solid-solution range from 45.2 to 47.0 at.% S. Above this temperature, the solid-solution range shrinks with increasing temperature, and the metal-rich composition varies. Finely, high-form pentlandite (Fe_{4.95}Ni_{4.06}S_{8.01}) melts as a pseudoperitectic reaction at 865 °C, changing to a mixture of monosulfide solid-solution and liquid as seen in the Figure.

Phase relations along the Fe_{0.9}S–Ni_{3}S_{2} join

We considered a pseudo-binary phase diagram for the Fe_{0.9}S–Ni_{3}S_{2} join, passing through the ideal composition of pentlandite in the system at temperatures from 600 to 950 °C, as shown Figure 8. On the this join, the phase relations below 650 °C are complicated and are described in a previous paper (Kitakaze et al. 2011).

Above 600 °C, the high-form pentlandite solid solution occupies the central portion of the join. Its field is granularly reduced and the Fe-rich end removed to the more Fe-rich side with increasing temperature. The high-form pentlandite melts incongruently by a pseudoperitectic reaction to a mixture of monosulfide solid solution and liquid.

Discussion

Pentlandite stability

No phase corresponding to high-form pentlandite solid solution including Fe_{4.5}Ni_{4.5}S_{8.0} was found at temperatures above 610 °C by Kullerud (1963a, b), Kullerud et al. (1969), or Hsieh et al. (1982). However, Sugaki et al. (1983, 1984) found an extensive field for high-form pentlandite with more Fe-rich compositions than Fe_{4.5}Ni_{4.5}S_{8.0} to Ni_{3±x}S_{2}
along the Ni–S boundary at 800 and 650 °C. Hayashi et al. (1985) and Hayashi (1985) also recognized the existence of this same solid solution in equilibrium experiments for the quaternary Cu–Fe–Ni–S system at 850 °C, and 800, 650, and 600 °C, respectively. Fedorova & Sinyakova (1993) investigated the isothermal phase relations in the Fe–Ni–S system at 900, 820, and 600 °C, and reported an extended heazlewoodite solid solution (Fe$_{x}$Ni$_{1-x}$)$_{3}$S$_{2}$ at 820 and 600 °C, with limited pentlandite solid solution. Karup-Møller & Makovicky (1995) showed an elongated field for (Fe,Ni)$_{3+z}$S$_{2}$ in the phase diagram at 725 °C. Both solid solutions correspond to the high-form pentlandite–Ni$_{3+z}$S$_{2}$ solid-solution of Sugaki et al. (1983, 1984) and Kitakaze et al. (2011).

A Ni-rich ternary phase (Ni,Fe)$_{3+z}$S$_{2}$ in the Ni-rich portion of the system was documented at 862 °C by Kullerud (1963b) and Kullerud et al. (1969). A ternary

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**Fig. 7.** The phase diagram of the sulfur composition versus the temperature with Fe–Ni in the Fe–Ni–S system with additional data from Sugaki & Kitakaze (1998) and Kitakaze et al. (2011). All phases and phase assemblages coexist with vapor. Abbreviations: See Table 1; liq = liquid.
phase \( b \) with a limited solid-solution at 850 °C was also described by Hsieh et al. (1982). However, these phases are located in the liquid field or along its S-rich boundary at 850 °C in this study, except for a small S-rich part of phase \( b \).

High-form pentlandite with composition \( \text{Fe}_{4.94}\text{Ni}_{4.06}\text{S}_{8.00} \) appears earliest at 870 ± 3 °C via a pseudoperitectic reaction between monosulfide solid solution and liquid in the system. This precipitation by the pseudoperitectic reaction terminates when the high-form solid solution extends its composition to reach the Ni–S join to include phase \( b_2 \) at 806 ± 3 °C. It is noticeable that the appearance of the high-form is so fast as to form the extensive solid solution on cooling in only 64 °C from 870 to 806 °C. After the pseudoperitectic reaction, the crystallization of the high-form from the liquid by pseudoeutectic reaction continues with decreasing temperature down to 739 ± 3 °C, at which point the tie-line of the liquid–high-form pentlandite changes into those of the \( b_1–\gamma \) phases. Fedorova & Sinyakova (1993) also stated that the heazlewoodite solid solution (high-form pentlandite solid solution) forms by a peritectic reaction between monosulfide solid solution and liquid below 876 °C. Karup-Møller & Makovicky (1995) suggested that liquid (sulfide melt)–monosulfide solid-solution fractionation is replaced by liquid–(Fe,Ni)\(_{3-x}\)S\(_2\) fractionation just below 850 °C, and this fractionation persists down to 635 °C, at which temperature the liquid in the Ni–S join solidifies (Kullerud & Yund 1962). According to our study, the tie-line between liquid and high-form pentlandite persists at temperatures from 870 ± 3 °C to 739 ± 3 °C, but no such tie-lines exist below 739 ± 3 °C. Similarly, liquid–monosulfide solid solution tie-lines persist down to 762 ± 3 °C, but no such tie-lines are found below this temperature.

**Pentlandite ore genesis**

High-form pentlandite with Fe=Ni can crystallize from liquid at temperatures from 865 to 746 °C. This suggests that the Ni-Cu sulfide ores with high-form pentlandite can form by crystallization from sulfide magma in the geological process, as supported by the observation and description in the previous literature (Lindgren 1933, 1937, Bateman 1952, Hawley 1962, Ramdohr 1980). From our experimental data and referring to previous papers for primary pentlandite genesis, we propose that pentlandite is formed by the following genetic processes: (1) transition (615 to 584 °C in Fe=Ni) from the high-form, crystallized primarily from sulfide magma by successive peritectic and eutectic reactions (for instance, at 870 to 739 °C in the system

![Fig. 8. The phase diagram of the pseudobinary from 0 to 60 at.% Ni in the Fe\(_{0.9}\)S–Ni\(_3\)S\(_2\) join in the Fe–Ni–S system. All phases and phase assemblages coexist with vapor. Abbreviation: See Table 1; liq = liquid.](image)

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