A REVISION OF PHASE RELATIONS IN THE SYSTEM 
Fe–Ni–S FROM 650° TO 450°C

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ABSTRACT

An elongate field of high-form pentlandite solid-solution, Fe$_5$Ni$_{3.35}$S$_{7.85}$, $\beta_2$ (Ni$_{4.32}$S$_{3}$), occurs in the system Fe–Ni–S at 650°C. This solid solution coexists with monosulfide solid-solution, $\beta_1$ (Ni,Fe)$_3$S$_2$ and $\gamma$ (Fe,Ni). Pentlandite with a composition Fe$_5$Ni$_{3.40}$S$_{7.82}$ first appears as a stable phase at 625°C owing to the phase transition of the most Fe-rich high-form pentlandite with the same composition. It grows as a limited solid-solution, from Fe$_5$Ni$_{3.36}$S$_{7.82}$ to Fe$_5$Ni$_{3.35}$S$_{7.92}$ at 600°C and from Fe$_5$Ni$_{3.32}$S$_{7.85}$ to Fe$_2$Ni$_{6.35}$S$_{7.85}$ at 500°C owing to a continuous phase-transition, exsolution and breakdown (pseudoperitectoid and pseudo-eutectoid) of the high-form solid-solution and the exsolution and breakdown (pseudo-eutectoid) of $\beta_1$. The compositional range of the solid solution is also increased by the exsolution of monosulfide solid-solution below 625°C. Pentlandite coexists with high-form pentlandite (625° to 503°C), monosulfide solid-solution (below 625°C), $\gamma$ (below 617°C) and $\beta_1$ (579° to 484°C). High-form pentlandite still remains stable below 520°C, but breaks down to pentlandite, high-form godlevskite and $\beta_1$ at 503° ± 3°C and Fe$_{1.04}$Ni$_{7.96}$S$_{6.93}$ (eutectoid). Phase $\beta_1$ also breaks down to pentlandite, heazlewoodite and $\gamma$ at 484° ± 3°C and Fe$_{0.26}$Ni$_{2.87}$S$_{2.00}$ (eutectoid). The assemblages with pentlandite and high-form godlevskite or heazlewoodite first appear at 568° ± 3°C or 498° ± 3°C, respectively. In this study, we show that pentlandite in the Ni–Cu ores can form at temperatures from 625° to 500°C or less owing to the phase transition, exsolution and eutectoid of the high-form pentlandite solid-solution, monosulfide solid-solution and $\beta_1$. These are the primary phases that would crystallize from sulfide magma (liquid in the system Fe–Ni–S) between around 1000° and 750°C.

Keywords: system Fe–Ni–S, pentlandite, godlevskite, monosulfide solid-solution, phase transitions, exsolution, phase equilibrium.

SOMMAIRE

La forme désordonnée de la solution solide pentlandite, Fe$_{5.65}$Ni$_{3.35}$S$_{7.85}$, $\beta_2$ (Ni$_{4.32}$S$_{3}$), occupe un champ de stabilité allongé dans le système Fe–Ni–S à 650°C. Cette solution solide coexiste avec une solution solide monosulfurée, $\beta_1$ (Ni,Fe)$_3$S$_2$ et $\gamma$ (Fe,Ni). La pentlandite ayant une composition Fe$_{5.66}$Ni$_{3.36}$S$_{7.82}$ est le premier représentant de la solution solide à apparaître à 625°C à cause d’une transition de phases de la composition la plus riche en fer de la pentlandite désordonnée ayant la même composition. Son champ augmente de façon limitée de Fe$_{5.66}$Ni$_{3.36}$S$_{7.82}$ à Fe$_{2.25}$Ni$_{5.75}$S$_{7.92}$ à 600°C et de Fe$_{5.68}$Ni$_{3.32}$S$_{7.85}$ à Fe$_{2.43}$Ni$_{6.35}$S$_{7.85}$ à 500°C en réponse à des transitions de phases continues, l’exsolution et la déstabilisation par relations pseudopéritéctoïdes et pseudo-eutéctoïdes) affectant la solution solide désordonnée, et l’exsolution et la déstabilisation (pseudo-eutéctoïde) de $\beta_1$. L’étendue de la composition de la solution solide augmente aussi par l’exsolution de la solution solide monosulfurée en dessous de 625°C. La pentlandite coexiste avec la pentlandite désordonnée (de 625° à 503°C), la solution solide monosulfurée (en dessous de 625°C), $\gamma$ (en dessous de 617°C) et $\beta_1$ (de 579° à 484°C). La pentlandite désordonnée demeure stable à moins de 520°C, mais se déstabilise pour donner pentlandite, godlevskite (forme de haute température) et $\beta_1$ à 503° ± 3°C et Fe$_{1.04}$Ni$_{7.96}$S$_{6.93}$ (eutectoid). La phase $\beta_1$ aussi se déstabilise pour donner pentlandite, heazlewoodite et $\gamma$ à 484° ± 3°C et Fe$_{0.26}$Ni$_{2.87}$S$_{2.00}$ (eutectoid). Les assemblages avec pentlandite et godlevskite de haute température ou heazlewoodite font leur apparition à 568° ± 3°C ou 498° ± 3°C, respectivement. Dans ce travail, nous démontrons que la pentlandite des minéraux Ni–Cu pourrait cristalliser sur un intervalle de température allant de 625° à 500°C ou moins comme résultat de transition de phase.

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exsolution and relations eutectoides impliquant la pentlandite désordonnée (solution solide), la solution solide monosulfurée et β₁. Celles-ci sont les phases primaires qui auraient cristallisé à partir d’un magma sulfuré (phase liquide du système Fe–Ni–S) entre environ 1000°C et 750°C.


**INTRODUCTION**

Since the study by Kullerud (1962, 1963a), it has been accepted that pentlandite (Fe₄.₅Ni₄.₅S₈) breaks down to a mixture of pyrrhotite (monosulfide solid-solution) and phase Ni₃₋₂S₂ at 610°C ± 3°C or above (Kullerud et al. 1969, Craig & Scott 1976, Barton & Skinner 1979, Craig & Vaughan 1981). However, Sugaki & Kitakaze (1992, 1998) found that pentlandite of composition Fe₄.₅Ni₄.₅S₇.₉ does not break down but transforms into a high form at 615°C ± 3°C, and that a continuous solid-solution between this high form and phase Ni₃₋₂S₂ is stable in the system Fe–Ni–S at 800°C and 650°C (Sugaki et al. 1982, 1984). Fedorova & Sinyakova (1993) reported an extended heazlewoodite solid-solution (FeₓNi₁₋ₓ)₁₃S₂ at 820°C and 600°C in the system Fe–Ni–S. Also, Karup-Møller & Makovicky (1995) ascertained the existence of an elongate solid-solution with composition (Ni,Fe)₃₋₂S₂ in the system at 725°C. Kosyakov et al. (1996) reported some schematic polythermal cross-sections in the system Fe–Ni–S at less than 50 mole % S, but no phase diagram for the ternary system was shown. Sinyakova & Kosyakov (2001) showed the 600°C section of the Fe–FeS–Ni–Ni phase diagram and recognized pentlandite, monosulfide solid-solution, heazlewoodite solid-solution and metal phases. But β₁ and β₂ in the binary system Ni–S described below were not found, so some problem has remained. Furthermore, Hayashi (1985) recognized the existence of a (Fe,Ni)₃₋₂S₂–Ni₃₋₂S₂ solid solution in his study of the quaternary system Cu–Fe–Ni–S at 850°C and 650°C. All of these solid solutions involve the same phases. Peregoedova & Ohnenstetter (2002) reported that a quaternary solid-solution between heazlewoodite solid-solution (Ni,Fe)₃₋₂S₂ and intermediate solid-solution Cu₁₋ₓFe₁ₓS₂ was established in the system Fe–Ni–Cu–S at 760°C.

On the other hand, Lin et al. (1978), Sharma & Chang (1980), Singleton et al. (1991) and Kitakaze & Sugaki (1996, 2001) found that phase Ni₃₋₂S₂ (β) (Kullerud & Yund 1962, Liné & Huber 1963, Rau 1976) in the binary system Ni–S is not a monophase but consists of two limited solid-solutions, phases β₁ (Ni₃₋₂S₂ corresponding to a high form of heazlewoodite) and β₂ (Ni₄S₃, a high-temperature phase), with a narrow field of immiscibility between them over the temperature range from 524°C to 806°C. Accordingly, the high-form pentlandite, Ni₃₋₂S₂ solid-solution mentioned above must be incorrect as it is possible for high-form pentlandite to form a continuous solid-solution with either β₁ or β₂, but not both.

The appearance of high-form pentlandite, β₁ and β₂ as stable phases required the re-examination and revision of the phase relations of the systems Fe–Ni–S and Cu–Fe–Ni–S above 500°C obtained by the previous authors (Kullerud 1963b, Kullerud et al. 1969, Craig & Kullerud 1969, Hsieh et al. 1982, Barker 1983, Hayashi 1985, Fedorova & Sinyakova 1993, Karup-Møller & Makovicky 1995, Peregoedova & Ohnenstetter 2002). In order to clarify the phase relations among high-form pentlandite, low-form pentlandite, β₁ and β₂ and their thermal stabilities, we have investigated seven isotherms in the system Fe–Ni–S at 50°C to 20°C intervals from 650°C to 450°C, especially where both high or low pentlandite (or both) and β₁ coexist. We have found several phase changes such as pseudoperitectoids, pseudoeutectoids, ternary peritectoids and eutectoids and tie-line changes in addition to a polymorphic phase-transition. As a result, the phase relations of the system have become more complicated than those described by the earlier investigators. Our experimental results are reported in this paper.

**EXPERIMENTAL PROCEDURES**

*Synthesis and equilibrium runs*

Chemical compositions and crystallographic data for minerals and solid phases appearing in this study are compiled in Table 1.

Synthesis experiments 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 precisely weighed to prepare the desired compositions of each run, and then sealed in a transparent silica-glass-tube under vacuum of 1.33 × 10⁻¹ Pa (10⁻³ Torr).

The sealed tubes with their charges were kept at 650°C, 600°C, 550°C, 520°C, 500°C, 470°C and 450°C for 25 to 40 days, after preheating at 400°C for three days. The products were ground and mixed under acetone in agate mortar in order to homogenize them thoroughly, resealed in an evacuated silica tube, and reheated at each temperature from 650°C to 450°C for 15 to 70 days. After reheating, the tubes were rapidly cooled in ice water.
The final products were aggregates of fine anhedral grains of the phases 5 to 50 μm in size (Table 1), except for S and liquid, which solidified upon cooling.

**Microscopic examination**

All the products of the runs were examined with a reflected light microscope. Among the products, pyrite, vaesite, monosulfide solid-solution, pentlandite, high-form godlevskite (α-Ni$_3$S$_2$; Fleet 1972), heazlewoodite and the metals, α (“kamacite” = iron), γ (taenite) and awaruite, which were homogeneous phases after quenching. The liquid crystallized upon cooling. High-form pentlandite, $\beta_1$ and $\beta_2$ were unquenchable. In general, they were not a monophase after quenching and consisted of cooling products that appeared as a consequence of phase transitions, eutectoid, peritectoid or exsolution reactions during cooling, as described below. Because of a very fine grain-size and weak contrast among phases of the run products, an examination with a back-scattered electron (BSE) image taken with an electron-probe microanalyzer (EPMA) was generally used in addition to an examination with reflected light microscopy.

Primary high-form pentlandite with Fe- and S-rich compositions (e.g., Fe$_{5.6}$Ni$_{3.3}$S$_{57.85}$ and Fe$_{5.2}$Ni$_{3.7}$S$_{8.05}$) in granular form (5 to 10 μm in size) and aggregates at 650°C changed to homogeneous pentlandite by inversion of the high form during cooling. However, most of the high-form pentlandite solid-solution except its Fe- and S-rich portion at temperatures from 650°C to 503°C was not homogeneous after quenching, but breaks down into a fine-grained aggregate of pentlandite, heazlewoodite and godlevskite, less than 2 μm in size, at room temperature.

Liquid occupies only a very small field at 650°C. On quenching, it developed a characteristic micrographic intergrowth (eutectic texture) of heazlewoodite as matrix and γ as fine lamellae, stringers and dots.

High-form pentlandite changes into pentlandite at room temperature, so they are indistinguishable under the microscope. However, high-form pentlandite [except for cases with a Fe- and S-rich composition] in general forms fine-grained quench products, and pentlandite is invariably homogeneous. These products can be distinguished on the basis of the presence or absence of quench products in the pentlandite matrix.

**High-temperature X-ray powder-diffraction**

Because high-form pentlandite and phases $\beta_1$ and $\beta_2$ are unquenchable, an X-ray powder diffractometer with a high-temperature heating unit was used for their identification. Pentlandite and high-form pentlandite can be distinguished from each other by their X-ray powder patterns, as shown by Sugaki & Kitakaze (1998). X-ray-diffraction patterns for small samples below 700°C, or at high temperatures above 700°C up to 900°C along the Ni–S boundary, were obtained by using an imaging plate X-ray diffractometer with a high-temperature heating unit.

**Electron-probe microanalysis (EPMA)**

The chemical compositions of the phases produced were obtained by EPMA with analytical conditions as

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**TABLE 1. CHEMICAL COMPOSITIONS AND CRYSTALLOGRAPHIC DATA OF MINERALS AND PHASES ENCOUNTERED IN THIS STUDY**

<table>
<thead>
<tr>
<th>Minerals and phases</th>
<th>Symbol</th>
<th>Formula</th>
<th>Structure type</th>
<th>Cell edges in Å</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrite</td>
<td>py</td>
<td>(Fe,Ni)S$_2$</td>
<td>Cubic Pa3</td>
<td>a 5.3825</td>
<td>Fuji et al. (1986)</td>
</tr>
<tr>
<td>Vaesite</td>
<td>vs</td>
<td>(Ni,Fe)$_2$S</td>
<td>Cubic Pa3</td>
<td>a 5.6765</td>
<td>Nowacki et al. (1991)</td>
</tr>
<tr>
<td>Violarite</td>
<td>vl</td>
<td>(Fe,Ni)$_2$S</td>
<td>Cubic Fd3m</td>
<td>a 9.465</td>
<td>Craig (1971)</td>
</tr>
<tr>
<td>Ni monosulfide</td>
<td>Nm</td>
<td>Ni$_3$S</td>
<td>Hexagonal P6$_3$/mmc</td>
<td>(x = 0) a 3.435, c 5.350</td>
<td>Futami &amp; Anzai (1984)</td>
</tr>
<tr>
<td>Monosulfide solid-solution</td>
<td>ms</td>
<td>(Fe,Ni)$_2$S</td>
<td>Hexagonal P6$_3$/mmc</td>
<td>(Fe = Ni) 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)$_2$S</td>
<td>Cubic Pn3m</td>
<td>a 5.245 (650°C)</td>
<td>This study</td>
</tr>
<tr>
<td>Pentlandite</td>
<td>pn</td>
<td>(Fe,Ni)$_2$S</td>
<td>Cubic Fm3m</td>
<td>(Fe = Ni) a 10.100</td>
<td>Rajamani &amp; Prewitt (1973)</td>
</tr>
<tr>
<td>High-form godlevskite</td>
<td>hgd</td>
<td>Ni$_3$S$_3$</td>
<td>Hexagonal</td>
<td>a 3.253, c 11.359 (550°C)</td>
<td>This study</td>
</tr>
<tr>
<td>Phase $\beta_1$</td>
<td>$\beta_1$</td>
<td>Ni$_3$S$_3$ (ss)</td>
<td>Cubic Pn3m</td>
<td>a 5.140 (600°C)</td>
<td>Kitakaze &amp; Sugaki (2001)</td>
</tr>
<tr>
<td>Phase $\beta_2$</td>
<td>$\beta_2$</td>
<td>Ni$_3$S$_3$ (ss)</td>
<td>Cubic Pn3m</td>
<td>a 5.210 (600°C)</td>
<td>Kitakaze &amp; Sugaki (2001)</td>
</tr>
<tr>
<td>Heazlewoodite</td>
<td>hz</td>
<td>Ni$_3$S$_3$</td>
<td>Hexagonal R32</td>
<td>a 5.747, c 7.135</td>
<td>Fleet (1977)</td>
</tr>
<tr>
<td>Phase $\alpha$ (“kamacite”)</td>
<td>$\alpha$</td>
<td>(Fe,Ni)Fe$<em>{0.88}$Ni$</em>{0.12}$</td>
<td>Cubic Fm3m</td>
<td>a 2.860</td>
<td>Ramsden &amp; Cameron (1966)</td>
</tr>
<tr>
<td>Phase $\gamma$ (taenite)</td>
<td>$\gamma$</td>
<td>(Fe,Ni)Fe$<em>{0.3}$Ni$</em>{0.70}$</td>
<td>Cubic Fm3m</td>
<td>a 3.587</td>
<td>Dumphie et al. (1987)</td>
</tr>
<tr>
<td>Awaruite</td>
<td>aw</td>
<td>FeNi$_2$ (ss)</td>
<td>Cubic Fm3m</td>
<td>a 3.555</td>
<td>Lufts &amp; Gielen (1970)</td>
</tr>
</tbody>
</table>

ss: solid solution. “Kamacite” is used in quotation marks because it has been discredited by the IMA. Iron is the revised name of this phase.
follows: accelerating voltage, 20 kV; specimen current, 0.010 μA; curved crystals, LiF for FeKα and NiKα, and TAP for SKα. Synthetic FeS and NiS were used as standards for Fe and S, and for Ni, respectively, in sulfides. Pure Fe and Ni metals (99.999%) were also as standards for Fe and Ni, respectively, in alloys (α, γ and awaruite).

Standard deviations 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, monosulfide solid-solution, pentlandite, high-form godlevskite, heazlewoodite, α, γ and awaruite; 2) ±0.3 wt% for the Fe and Ni, and ±0.4 wt% for S of the phases with fine-grained quench products such as high-form pentlandite, β₁ and β₂, and 3) ±0.4 wt% for Fe and Ni, and ±0.5 wt% for S of liquid. However, high-form pentlandite, which inverts to homogeneous pentlandite (low form) on cooling, has standard deviations of ±0.1 wt% for Fe, Ni and S.

The chemical formulae Fe₃NiS₄ of sulfide, liquid and metal (alloy) phases in this paper indicate the atomic values converted from EPMA data as follows: z = 6.00 for high-form godlevskite; z = 4.00 for violarite; z = 3.00 for Fe-free β₂; z = 2.00 for vaesite, pyrite, heazlewoodite and β₁; z = 1.00 for monosulfide solid-solution; x + y = 9.00 for high-form pentlandite, Fe-bearing β₂ and pentlandite; x + y + z = 10.0 for liquid, and x + y = 10.0 (z = 0) for metals such as α (iron, “kamacite”), γ (taenite) and awaruite (FeNi₃).

**Differential thermal analysis (DTA)**

Differential thermal analysis, with an evacuated silica-glass tube as a reaction vessel was performed to obtain temperatures of reactions causing phase changes such as liquidus, peritectic, eutectic, eutectoid, peritectoid, polymorphic phase-transitions and tie-line change in the phase diagram. The heating rate of the DTA was generally fixed at 5°C/min from room temperature to 900°C or 1000°C, but frequently a slower heating or cooling rate of 2°C, 1°C or 0.3°C/min from 400°C to 850°C or 850°C to 400°C, respectively, was used to determine more accurately the temperatures of the thermal reactions. Temperatures were calibrated using the melting or freezing points of high-purity tin (231.97°C), zinc (419.6°C), aluminum (660.4°C) and silver (961.9°C).

**Experimental Results**

**Phases β₁ and β₂ on the Ni–S binary and their phase relations**

The extensive solid-solution field of phase Ni₃₃₃S₂ previously determined (Rosenqvist 1954, Kullerud & Yund 1962, Liné & Huber 1963) as high-form heazlewoodite in the binary Ni–S is not a monophase (Rau 1976), but consists of two limited solid-solutions, β₁ and β₂ with a narrow field of immiscibility between them, as determined by S activity measurement using a H₂S–H₂ gas equilibrium technique by Lin *et al.* (1978). This fact was furthermore recognized by Sharma & Chang (1980) and Singleton *et al.* (1991). However, no crystal data were given for β₁ and β₂. To reconfirm the existence of the phases β₁ and β₂ and to obtain the relevant crystal data, high-temperature X-ray powder-diffraction was performed on synthetic Ni₃S₂ (β₁) and Ni₃S₃ (β₂) at temperatures from 500° to 700°C, because both β₁ and β₂ are unquenchable (Kitakaze & Sugaki 1996, 2001). Accordingly, β₁ and β₂ can be distinguished from each other by the difference of their powder-diffraction patterns. The phase β₁ (Ni₃S₂) is cubic Fm3m with a equal to 5.210 Å (600°C). The phase β₂ (Ni₃S₃) is cubic Pn3m with a equal to 5.140 Å (600°C).

The phase relations for the Ni–S binary above 400°C for compositions between 32.0 and 54.0 at.% S, including β₁, β₂, high-form godlevskite and Ni monosulfide, were re-examined using high-temperature X-ray powder-diffraction, DTA and microscopy. The resulting phase-diagram (Fig. 1) is modified from that obtained by Kitakaze & Sugaki (2001), who referred to data of Kullerud & Yund (1962), Lin *et al.* (1978), Sharma & Chang (1980) and Singleton *et al.* (1991). The appearance of solid phases was primarily monitored by high-temperature X-ray powder-diffactometry up to 700°C. Phase identification above this temperature up to 900°C was performed using the IP X-ray diffractometer with a high-temperature unit.

Two limited solid-solutions of β₁ and β₂ with a narrow immiscible field between them were found in place of the phase Ni₃₃₃S₂ (Fig. 1). The cell edges of the β₁ and β₂ solid-solutions decrease linearly with increasing S content (Kitakaze & Sugaki 2001). The phase β₁ at its most S-rich composition (43.0 atomic % S) breaks down to β₂ (43.3 at.% S) and liquid (42.7 at.% S) at 800°C, whereas β₂ at its most S-rich composition (44.5 at.% S) breaks down to Ni monosulfide (50.3 at.% S) and liquid (43.7 at.% S) at 806° ± 3°C. On cooling, there is a eutectic point at 637° ± 3°C and 33.2 at.% S between the β₁ (36.7 at.% S) and Ni (Lin *et al.* 1978, Singleton *et al.* 1991). The liquid disappears below this temperature. The phase β₁ with Ni₃S₂ (40.0 at.% S) inverts to heazlewoodite (low form) at 565° ± 3°C. This transition is reversible. Also, β₁ compositions with 40.6 and 37.0 at.% S break down to mixtures of heazlewoodite (40.0 at.% S) and β₂ (~41.5 at.% S) at 564° ± 3°C and heazlewoodite and Ni (~0.0 at.% S) at 533° ± 3°C, respectively, at two eutectoid reactions. Phase β₂ with 43.0 at.% S breaks down to a mixture of heazlewoodite and high-form godlevskite at 524° ± 3°C at another eutectoid.

High-form godlevskite of a composition Ni₆₀S₆₀ crystallizes as a result of a peritectoid reaction between β₂ and Ni monosulfide at 573° ± 3°C, and grows to a...
slightly metal-rich side as a limited solid-solution from 45.3 to 46.1 at.% S at 524°C, at which is a eutectoid of \( \beta_2 \), but decreases its extent of solubility gradually with decreasing temperature. It coexists with \( \beta_2 \) from 573°C to 524°C, with heazlewoodite from 524°C to 400°C in the Ni-rich field, and Ni monosulfide from 573°C to 397°C in the S-rich field (Fig. 1).

Phase relations in the Fe–Ni–S system at 650°C

High-form pentlandite \( (\text{Fe}_{4.93}\text{Ni}_{4.07}\text{S}_{8.01}) \) first crystallized as a product of a peritectic reaction between monosulfide solid-solution and liquid at 870°C ± 3°C, forms as a limited solid-solution from \( \text{Fe}_{5.06}\text{Ni}_{4.94}\text{S}_{7.92} \) to \( \text{Fe}_{3.79}\text{Ni}_{5.21}\text{S}_{7.92} \), and includes the ideal composition \( \text{Fe}_{4.50}\text{Ni}_{4.50}\text{S}_{8.00} \) of pentlandite at 850°C in the system Fe–Ni–S (Sugaki & Kitakaze 1998, 2006). This solid-solution field extends rapidly toward the Ni-rich side with decreasing temperature and reaches Fe-free \( \beta_2 \) (44.5 at.% S) on the Ni–S boundary at 806°C (Fig. 1), where phase \( \beta_2 \) crystallizes according to a peritectic reaction between Ni monosulfide and liquid (Lin et al. 1978, Kitakaze & Sugaki 2001). Consequently, a continuous solid-solution from Fe-rich high-form pentlandite \( (\text{Fe}_{5.23}\text{Ni}_{3.77}\text{S}_{7.89}) \) at 800°C) to \( \beta_2 \) of composition \( \text{Ni}_{3.74}\text{S}_{3.00} \) is formed at 806°C (Sugaki & Kitakaze 1996). This high-form pentlandite \( \beta_2 \) solid-solution is hereafter referred to as high-form pentlandite solid-solution.

The equilibrium-run data and the EPMA data for the synthetic products were used to draw a phase diagram for the ternary system Fe–Ni–S at 650°C, as shown in Figure 2. Pyrite, vaesite, monosulfide solid-solution, high-form pentlandite solid-solution, \( \beta_1 \), \( \gamma \), \( \alpha \), liquid (sulfide) and S (liquid) occur as stable phases in the system. Monosulfide solid-solution forms a complete solid-solution between \( \text{Fe}_{1-x}\text{S} \) and \( \text{Ni}_{1-x}\text{S} \). It coexists with pyrite or vaesite (or both) on the S-rich side, and...
high-form pentlandite solid-solution on the metal-rich side except for the most Fe-rich part of the system, where it coexists with γ or α (or both). High-form pentlandite solid-solution appears as an elongate field extending from β₂ of composition Ni₃.₇₉–₄.₀₂S₃.₀₀ at the Ni–S boundary, and coexists with γ or β₁ in the Fe- and Ni-rich portions, respectively, on the metal-rich side. The composition of the most Fe-rich high-form solid-solution is Fe₅.₆₅Ni₃₃S₇.₈₅. This solid solution also includes the composition of Fe₄.₅Ni₄₅S₈₈ as S-rich extremity around Fe = Ni in atomic %. The liquid phase occupies an extensive field at 850°C (Sugaki & Kitakaze 1998), but its area is remarkably reduced with decreasing temperature, although it still retains a very small field jutting out within the ternary from the Ni–S boundary at 650°C. The field of β₁ appears independently as a horn-shaped solid-solution of compositions from Ni₂.₇₈–₃.₂₉S₂.₀₀ to Fe₀.₅₆Ni₂.₃₄S₂.₀₀ projected within the ternary system from the Ni–S boundary; it coexists with high-form pentlandite solid-solution, γ and liquid.

In the metal-rich portion of the system, four univariant assemblages are found as follows: 1) monosulfide solid-solution (Fe₀.₉₉Ni₀₁S₁.₀₀) + α (Fe₉.₅₃Ni₀₄.₄₇) + γ (Fe₈.₅₄Ni₁.₄₆) (Kubaschewski 1982, Swartzendruber et al. 1993), 2) high-form pentlandite (Fe₅.₆₅Ni₃₃S₇.₈₅) + monosulfide solid-solution (Fe₀.₈₅Ni₀.₁₃S₁.₀₀) + γ (Fe₃.₅₈Ni₆.₄₂), 3) high-form pentlandite (Fe₂.₆₁Ni₆.₃₉S₆.₉₉) + β₁ (Fe₀.₅₆Ni₂.₃₄S₂.₀₀) + γ (Fe₂.₈₀Ni₇.₃₀), and 4) β₁ (Fe₀.₅₀Ni₂.₉₀S₂.₀₀) + liquid (Fe₀.₅₀Ni₆.₀₈S₃.₄₂) + γ (Fe₂.₀₀Ni₈.₀₀), all in the presence of an equilibrium vapor.

Also, in the S-rich portion of the ternary, there are two univariant assemblages, 5) or 6), pyrite (Fe₀.₉₁Ni₀.₀₈S₂.₀₀) + vaesite (Fe₀.₁₉Ni₀.₈₁S₂.₀₀) + monosulfide solid-solution (Fe₀.₆₆Ni₂.₂₀S₁.₀₀) or S (liquid), respectively, in the presence of vapor.

**Phase relations from 650°C to 600°C**

The liquid field disappears entirely at 637°C and 33.2 at.% S eutectic on the Ni–S boundary (Fig. 1). Pentlandite (low form) first appears as a stable phase at 625°C ± 3°C as a result of a polymorphic phase-transition from high-form pentlandite solid-solution of the most Fe-rich composition Fe₅.₆₀Ni₃.₄₀S₇.₈₂. This reaction is reversible. The phase transition was documented by high-temperature X-ray powder diffraction, DTA, EPMA and microscopic examination (Sugaki & Kitakaze 1998). It proceeds toward the more Ni-rich or S-poor portions (or both) of the solid solution with decreasing temperature progressively, and as a result low-form pentlandite is formed as another solid-

![Fig. 2. The isothermal phase-diagram in the Fe–Ni–S system at 650°C. Symbols: see Table 1, liq: liquid, S(liq): sulfur liquid.](image)
solution. Meanwhile, the Fe-rich extremity of high-form pentlandite retreats toward the Ni-rich and S-poor sides with decreasing temperature.

The Fe-rich extremity of the pentlandite solid-solution shifts a little to the Fe-rich side by peritectoid and pseudoperitectoid reactions between monosulfide solid-solution and the Fe-rich extremity of high-form pentlandite solid-solution with decreasing temperature from 625°C. Because of the retreat of the high-form solid-solution and a slight growth of the Fe-rich extremity of pentlandite solid-solution with decreasing temperature, new tie-lines between the most Fe-rich end of pentlandite and γ occur at or below 617° ± 3°C, replacing those between monosulfide solid-solution and the Fe-rich end of high-form pentlandite solid-solution, which were stable above this temperature. This tie-line change was ascertained by microscopic examination, high-temperature X-ray diffraction and DTA.

On the other hand, the Ni-rich extremity of pentlandite solid-solution grows to the more Ni-rich side by a peritectoid reaction between monosulfide solid-solution (Fe$_{0.40}$Ni$_{0.57}$S$_{1.00}$) and high-form pentlandite (Fe$_{3.25}$Ni$_{5.75}$S$_{7.92}$) immediately after leaving the S-rich boundary of high-form pentlandite at 603°C and by a pseudoperitectoid reaction between them successively down to 568°C.

Phase relations at 600°C

The phase relations based on the data of the equilibrium experiments and the EPMA data at 600°C are shown in Figure 3. High-form pentlandite solid-solution still remains stably in the elongate field with compositions from Fe$_{5.28}$Ni$_{3.72}$S$_{7.54}$ to Ni$_{2.56-2.75}$S$_{3.00}$ ($\beta_2$), although it retreats toward the Ni–S boundary compared to its composition at 650°C. Pentlandite forms a limited solid-solution with a composition range from Fe$_{5.64}$Ni$_{3.36}$S$_{7.82}$ to Fe$_{3.25}$Ni$_{5.75}$S$_{7.92}$, including Fe$_{4.50}$Ni$_{4.50}$S$_{8.00}$ at 600°C. Therefore, both high- and low-form pentlandites coexist. The S-rich side of pentlandite solid-solution coexists with monosulfide solid-solution. Its metal-rich side coexists mostly with the high-form solid-solution. Only the Fe-rich portion of the pentlandite can coexist with γ because of the retreat of the field of the high-form solid-solution. The continuous monosulfide solid-solution still remains.

The field of $\beta_1$ becomes smaller at 600°C than at 650°C by shrinking and retreating toward the Ni–S boundary. It coexists with Ni-rich high-form pentlandite solid-solution or γ (or both).

In the metal-rich portion of the system, there are five univariant assemblages as follows: 1) monosulfide solid-solution (Fe$_{0.99}$Ni$_{0.01}$S$_{1.00}$) + α (Fe$_{9.48}$Ni$_{0.52}$)
Phase relations from 600° to 550°C

The high-form pentlandite solid-solution retreats rapidly toward the Ni–S boundary with decreasing temperature from 600°C, breaking down to a mixture of high-form pentlandite with a little Ni-rich composition + pentlandite + γ at another pseudoeutectoid reaction with decreasing temperature from 579° to 503° ± 3°C (ternary eutectoid of high-form pentlandite).

The Ni-rich extremity of the pentlandite solid-solution grows to the Ni-rich side by peritectoid and pseudoperitectoid reactions between monosulfide solid-solution and high-form pentlandite with decreasing temperature from 603° to 568°C. This pseudoperitectoid reaction in the phase diagram is expressed as the univariant assemblages monosulfide solid-solution, pentlandite and high-form pentlandite. These assemblages move to the Ni-rich side with decreasing temperature down to 568°C. The compositions of the Ni-rich extremity of pentlandite and monosulfide solid-solution and of high-form pentlandite covary as pairs of reactants as the pseudoperitectoids evolve at temperatures from 600° to 570°C.

The tie-lines between monosulfide solid-solution and high-form pentlandite are replaced by those between high-form godlevskite and pentlandite solid-solution at 568° ± 3°C. Thus, the high-form pentlandite solid-solution cannot coexist with monosulfide solid-solution below this temperature.

High-form godlevskite (α-Ni₁S₆ of Kullerud & Yund 1962, Misra & Fleet 1973a) of a composition with Fe₀.₁₂Ni₆.₉₀S₆.₀₀ (0.9Fe, 53.0Ni, 46.1S in at.%) first appears in the ternary field close to the Ni–S boundary, not on the Ni–S join, by a peritectoid reaction between monosulfide solid-solution (Fe₀.₀₁Ni₀.₉₀S₁.₀₀) and high-form pentlandite (Fe₀.₀₁Ni₈.₉₇S₇.₀₄) at 596° ± 3°C. It gets to the Ni–S boundary at 573° ± 3°C (Kullerud & Yund 1962), and also grows to the Fe-rich side conversely as a limited solid-solution (Fe₀.₂₃Ni₆.₇₈S₆.₀₀, 1.8 atomic % Fe) at 568°C with decreasing temperature by a pseudoperitectoid reaction between monosulfide solid-solution and high-form pentlandite at temperatures from 596° to 568°C, and furthermore extends continuously to the composition with Fe₀.₄₀Ni₆.₆₅S₆.₀₀ (3.1Fe, 50.8Ni, 46.1S in at.%) of maximum Fe content by pseudoeutectoid reactions of monosulfide solid-solution or high-form pentlandite at temperatures from 568° to 503°C.

Heazlewoodite first appears by inversion of β₁ (Ni₁S₂) at 565° ± 3°C, and then by exsolution subsequently from the solid solutions β₁ and β₂ on cooling from 565° to 533°C (eutectoid of Ni-rich β₁) and from 564° (eutectoid of S-rich β₁) to 524°C (eutectoid of β₂), respectively, at the Ni–S boundary (Fig. 1). This phase also occurs together with β₂ (Fe-free high-form pentlandite) at a S-rich eutectoid of β₁ at 564°C and 40.6 at.% S on the boundary, and grows as a small solid-solution within the ternary system, coexisting with Ni-rich high-form pentlandite (Fe-bearing β₂) and β₁ (Fe-bearing β₁) as a limited solid-solution below this temperature.
Phase relations at 550°C

An isothermal phase-diagram obtained from the experimental data at 550°C is shown in Figure 4. Because of the tie-line changes at 579° and 568°C and the appearance of high-form godlevskite at 596°C and heazlewoodite at 565°C on cooling as described above, the phase relations in the Ni-rich portion of the metal-rich field of the diagram become more complicated than those at 600°C (Fig. 3).

Pentlandite grows as a solid-solution from Fe_{5.68}Ni_{3.32}S_{7.84} to Fe_{2.44}Ni_{6.56}S_{7.85} at 550°C and coexists with monosulfide solid-solution, high-form pentlandite, high-form godlevskite, β₁ and γ. However, an assemblage of pentlandite and heazlewoodite cannot form because of the stable tie-lines between high-form pentlandite and β₁ at this temperature. Elongate high-form pentlandite solid-solution retreats further to the Ni-rich side, but still persists in a reduced field with compositions from Fe_{2.62}Ni_{6.38}S_{7.16} to Ni_{3.91–4.13}S_{3.00} (β₂) at 550°C. It coexists with high-form godlevskite, β₁ or heazlewoodite (or both) besides pentlandite. A β₁ field shrinks and deforms, but its Ni-rich portion still connects with the Ni–S boundary. High-form godlevskite appears as a limited solid-solution of composition from Ni_{7.00–7.04}S_{6.00} to Fe_{0.29}Ni_{6.76}S_{6.00}.

Heazlewoodite also is a phase with the composition from Ni_{3}S_{2} to Fe_{0.06}Ni_{2.95}S_{3.00} within the ternary system from the Ni–S boundary. Five new univariant assemblages, 1) monosulfide solid-solution (Fe_{0.19}Ni_{0.78}S_{1.00}) + pentlandite (Fe_{2.44}Ni_{6.56}S_{7.85}) + high-form godlevskite (Fe_{0.29}Ni_{6.76}S_{6.00}), 2) pentlandite (Fe_{2.44}Ni_{6.56}S_{7.85}) + high-form pentlandite (Fe_{1.79}Ni_{7.21}S_{7.27}) + high-form godlevskite (Fe_{0.29}Ni_{6.76}S_{6.00}), 3) pentlandite (Fe_{4.10}Ni_{4.90}S_{7.73}) + high-form pentlandite (Fe_{2.62}Ni_{6.38}S_{7.16}) + β₁ (Fe_{0.36}Ni_{2.63}S_{2.00}), 4) high-form pentlandite (Fe_{0.28}Ni_{8.72}S_{6.08}) + heazlewoodite (Fe_{0.06}Ni_{9.52}S_{5.00}) + β₁ (Fe_{0.14}Ni_{2.74}S_{2.00}), and 5) pentlandite (Fe_{4.39}Ni_{14.61}S_{7.70}) + β₁ (Fe_{0.41}Ni_{2.70}S_{2.00}) + γ (Fe_{3.47}Ni_{6.55}) appear, in contrast with the isotherm at 600°C. Other univariant assemblages, 6) monosulfide solid-solution (Fe_{0.99}Ni_{0.01}S_{1.00}) + α (Fe_{9.46}Ni_{0.54}) + γ (Fe_{7.61}Ni_{2.39}) and 7) monosulfide solid-solution (Fe_{0.89}Ni_{0.08}S_{1.00}) + pentlandite (Fe_{5.68}Ni_{3.32}S_{7.84}) + γ (Fe_{3.74}Ni_{6.26}) in the metal-rich portion, and 8) pyrite (Fe_{0.97}Ni_{0.04}S_{2.00}) + vaesite (Fe_{0.07}Ni_{0.92}S_{2.00}) + monosulfide solid-solution (Fe_{0.53}Ni_{0.30}S_{1.00}) or S (liquid) in the S-rich portion still exist stably, as those at 600°C, but the composition of each phase of the assemblages differ from those at 600°C.
Phase relations from 550° to 500°C

Phase $\beta_1$ disappears at 533° ± 3°C and 37.0 at. % S (metal-rich eutectoid) to break down to a mixture of heazlewoodite and Ni on the Ni–S boundary. However, it still persists stably as a ternary phase away from the Ni–S boundary at 520°C (Fig. 5). The phase $\beta_1$ coexists with pentlandite, high-form pentlandite (Fe-bearing $\beta_2$), heazlewoodite and $\gamma$ (or both), but does not associate with high-form godlevskite because of the stable tie-lines between high-form pentlandite and heazlewoodite at 520°C. Phase $\beta_2$ breaks down to a mixture of heazlewoodite and Ni on the Ni–S boundary. However, it still persists stably as a ternary phase away from the Ni–S boundary at 520°C (Fig. 5). The phase $\beta_2$ coexists with pentlandite, high-form pentlandite (Fe-bearing $\beta_2$), heazlewoodite and $\gamma$ (or both), but does not associate with high-form godlevskite because of the stable tie-lines between high-form pentlandite and heazlewoodite at 520°C. Phase $\beta_1$ breaks down to a mixture of heazlewoodite and Ni on the Ni–S boundary.

Seven univariant assemblages in the Ni-rich side of the system at 520°C are found in Figure 5, as follows:

1. pentlandite (Fe$_{2.40}$Ni$_{6.60}$S$_{7.89}$) + monosulfide solid-solution (Fe$_{0.15}$Ni$_{0.82}$S$_{1.00}$) + high-form godlevskite (Fe$_{0.42}$Ni$_{6.65}$S$_{6.00}$),
2. pentlandite (Fe$_{2.44}$Ni$_{6.56}$S$_{7.85}$) + high-form pentlandite (Fe$_{1.10}$Ni$_{7.90}$S$_{6.96}$) + high-form godlevskite (Fe$_{0.42}$Ni$_{6.65}$S$_{6.00}$),
3. pentlandite (Fe$_{3.52}$Ni$_{5.48}$S$_{7.82}$) + high-form pentlandite (Fe$_{1.32}$Ni$_{7.63}$S$_{6.85}$) + $\beta_1$ (Fe$_{0.36}$Ni$_{2.70}$S$_{2.00}$),
4. pentlandite (Fe$_{4.25}$Ni$_{4.75}$S$_{6.73}$) + $\beta_1$ (Fe$_{0.36}$Ni$_{2.75}$S$_{2.00}$) + $\gamma$ (Fe$_{3.48}$Ni$_{6.52}$),
5. high-form godlevskite (Fe$_{0.09}$Ni$_{6.98}$S$_{6.00}$) + high-form pentlandite (Fe$_{0.47}$Ni$_{8.53}$S$_{6.82}$) + heazlewoodite (Fe$_{0.04}$Ni$_{2.95}$S$_{3.00}$),
6. high-form pentlandite (Fe$_{0.54}$Ni$_{8.46}$S$_{6.82}$) + $\beta_1$ (Fe$_{0.20}$Ni$_{2.61}$S$_{2.00}$) + heazlewoodite (Fe$_{0.19}$Ni$_{2.90}$S$_{2.00}$),
7. $\beta_1$ (Fe$_{0.12}$Ni$_{3.22}$S$_{2.00}$) + heazlewoodite (Fe$_{0.01}$Ni$_{3.00}$S$_{2.00}$) + $\gamma$ (Fe$_{2.98}$Ni$_{7.02}$).

Awaruite (Fe$_{2.80}$Ni$_{7.20}$) appears as a result of an order–disorder transformation of $\gamma$ at 517°C and has a limited solid-solution extending along the Fe–Ni boundary with decreasing temperature (Kubaschewski 1982, Swartzendruber et al. 1993). It coexists with heazlewoodite or $\gamma$ (or both) below 517°C.

The tie-lines between high-form pentlandite and heazlewoodite are replaced by those between high-form godlevskite and $\beta_1$ at 512° ± 3°C or below. This tie-
Phase relations in the system Fe–Ni–S from 650° to 450°C

Line change was ascertained by DTA, high-temperature X-ray diffraction and microscopic examination.

The high-form pentlandite solid-solution finally breaks down to a mixture of pentlandite, \( \beta_1 \) and high-form godlevskite at 503° ± 3°C in a ternary eutectoid (invariant) and disappears completely below this temperature. This reaction was documented with DTA data, high-temperature X-ray diffraction and microscopic examination of run products. The composition of the high-form pentlandite at the eutectoid, 503°C, is almost the same as composition \( \text{Fe}_{1.04}\text{Ni}_{7.96}\text{S}_{6.93} \), and the compositions of its breakdown products also are very close to \( \text{Fe}_{2.44}\text{Ni}_{6.56}\text{S}_{7.85} \) for pentlandite, \( \text{Fe}_{0.20}\text{Ni}_{6.61}\text{S}_{6.00} \) for \( \beta_1 \) and \( \text{Fe}_{0.40}\text{Ni}_{6.61}\text{S}_{6.00} \) for high-form godlevskite at 500°C, obtained from the EPMA data.

Phase relations at 500°C

At 500°C, high-form pentlandite disappears, and pentlandite is present as an elongate solid-solution extending from \( \text{Fe}_{5.68}\text{Ni}_{3.32}\text{S}_{7.85} \) to \( \text{Fe}_{2.43}\text{Ni}_{6.57}\text{S}_{7.85} \), and coexists with monosulfide solid-solution, high-form godlevskite, \( \beta_1 \) or \( \gamma \) (or both), as shown in Figure 6. Pentlandite cannot coexist with heazlewoodite because of the stable tie-lines between high-form godlevskite and \( \beta_1 \) at 500°C. The monosulfide solid-solution field becomes narrower but still extends continuously across the entire diagram. High-form godlevskite coexists with \( \beta_1 \) or heazlewoodite (or both) in addition to monosulfide solid-solution or pentlandite (or both), but cannot coexist with \( \gamma \) or awaruite owing to the tie-lines of \( \beta_1 \) and pentlandite or heazlewoodite. Heazlewoodite coexists stably with \( \gamma \) or awaruite (or both) as well as \( \beta_1 \) or high-form godlevskite (or both). Awaruite coexists only with heazlewoodite or \( \gamma \) (or both) at 500°C. There are nine univariant assemblages (Fig. 6) in the metal-rich portion of the system, as follows: 1) monosulfide solid-solution \( \text{Fe}_{0.99}\text{Ni}_{0.01}\text{S}_{1.00} \) + \( \alpha \) \( \text{Fe}_{9.43}\text{Ni}_{0.57} \) + \( \gamma \) \( \text{Fe}_{7.04}\text{Ni}_{2.96} \) (Kubaschewski 1982, Swartzen druber et al. 1993), 2) pentlandite \( \text{Fe}_{5.68}\text{Ni}_{3.32}\text{S}_{7.85} \) + monosulfide solid-solution \( \text{Fe}_{0.92}\text{Ni}_{0.04}\text{S}_{1.00} \) + \( \gamma \) \( \text{Fe}_{4.20}\text{Ni}_{5.80} \), 3) pentlandite \( \text{Fe}_{2.43}\text{Ni}_{6.57}\text{S}_{7.85} \) + monosulfide solid-solution \( \text{Fe}_{1.33}\text{Ni}_{6.84}\text{S}_{1.00} \) + high-form godlevskite \( \text{Fe}_{0.40}\text{Ni}_{6.61}\text{S}_{6.00} \), 4) pentlandite \( \text{Fe}_{2.44}\text{Ni}_{6.56}\text{S}_{7.85} \) + high-form godlevskite \( \text{Fe}_{0.40}\text{Ni}_{6.61}\text{S}_{6.00} \) + \( \beta_1 \) \( \text{Fe}_{0.20}\text{Ni}_{2.70}\text{S}_{2.00} \), 5) high-form godlevskite \( \text{Fe}_{0.34}\text{Ni}_{6.70}\text{S}_{6.00} \) + \( \beta_1 \) \( \text{Fe}_{0.20}\text{Ni}_{2.70}\text{S}_{2.00} \) + heazlewoodite \( \text{Fe}_{1.33}\text{Ni}_{6.84}\text{S}_{1.00} \), 6) pentlandite \( \text{Fe}_{3.79}\text{Ni}_{5.21}\text{S}_{7.76} \) + \( \beta_1 \) \( \text{Fe}_{3.01}\text{Ni}_{2.81}\text{S}_{2.00} \) + \( \gamma \) \( \text{Fe}_{3.80}\text{Ni}_{6.20} \), 7) heazlewoodite \( \text{Fe}_{0.13}\text{Ni}_{6.84}\text{S}_{1.00} \) + \( \beta_1 \) \( \text{Fe}_{0.25}\text{Ni}_{2.70}\text{S}_{2.00} \) + \( \gamma \) \( \text{Fe}_{3.48}\text{Ni}_{6.57} \), 8) heazlewoodite \( \text{Fe}_{0.10}\text{Ni}_{2.93}\text{S}_{2.00} \) + \( \gamma \) \( \text{Fe}_{3.43}\text{Ni}_{6.57} \) + awaruite.

Fig. 6. The phase diagram in the Fe–Ni–S system at 500°C. See Table 1 for symbols, S(liq): sulfur liquid.
Meanwhile, in the S-rich portion of the system, pyrite (Fe$_{0.99}$Ni$_{0.02}$S$_{2.00}$) and vaesite (Fe$_{0.01}$Ni$_{0.99}$S$_{2.00}$) at 500°C still form two univariant assemblages with 10) monosulfide solid-solution (Fe$_{0.45}$Ni$_{0.47}$S$_{1.00}$) or S (liquid) as they do at higher temperature, although their solid-solution fields have shrunk.

**Phase relations from 500° to 450°C**

The tie-lines between $\beta_1$ and high-form godlevskite are replaced by those between pentlandite and heazlewoodite at 498° ± 3°C. This tie-line change was documented by DTA, high-temperature X-ray diffraction and microscopic examination. Pentlandite is able to coexist stably with heazlewoodite below this temperature. The $\beta_1$ field contracts with decreasing temperature, and finally disappears by its breakdown to a mixture of pentlandite, heazlewoodite and $\gamma$ at 484° ± 3°C at a ternary eutectoid. The composition of the $\beta_1$ at this eutectoid is very close to that of the $\beta_1$ (Fe$_{0.26}$Ni$_{2.87}$S$_{2.00}$) produced at 485° ± 3°C. Also, the compositions of the breakdown products at the eutectoid are close to those of pentlandite (Fe$_{3.23}$Ni$_{5.77}$S$_{7.76}$), heazlewoodite (Fe$_{0.11}$Ni$_{2.90}$S$_{2.00}$), and $\gamma$ (Fe$_{3.49}$Ni$_{6.51}$) at 482°C.

The isotherm of the system at 470°C are shown in Figure 7. The phase relations are simpler than those at 500° and 450°C because of disappearance of $\beta_1$ and the lack of crystallization of violarite. We found nine univariant assemblages, as follows: 1) monosulfide solid-solution (Fe$_{0.99}$Ni$_{0.01}$S$_{2.00}$) + $\alpha$ (Fe$_{0.45}$Ni$_{0.55}$) + $\gamma$ (Fe$_{0.45}$Ni$_{3.55}$), 2) monosulfide solid-solution (Fe$_{0.92}$Ni$_{0.04}$S$_{1.00}$) + pentlandite (Fe$_{5.70}$Ni$_{13.30}$S$_{7.85}$) + $\gamma$ (Fe$_{4.56}$Ni$_{5.44}$), 3) pentlandite (Fe$_{2.62}$Ni$_{6.38}$S$_{7.82}$) + monosulfide solid-solution (Fe$_{0.13}$Ni$_{0.85}$S$_{1.00}$) + high-form godlevskite (Fe$_{0.10}$Ni$_{6.86}$S$_{6.00}$), 4) pentlandite (Fe$_{0.02}$Ni$_{6.38}$S$_{7.82}$) + high-form godlevskite (Fe$_{0.16}$Ni$_{6.86}$S$_{6.00}$) + heazlewoodite (Fe$_{0.08}$Ni$_{2.92}$S$_{2.00}$), 5) pentlandite (Fe$_{3.44}$Ni$_{5.56}$S$_{7.76}$) + heazlewoodite (Fe$_{0.08}$Ni$_{2.92}$S$_{2.00}$) + $\gamma$ (Fe$_{4.16}$Ni$_{5.84}$), 6) heazlewoodite (Fe$_{0.06}$Ni$_{2.92}$S$_{2.00}$) + pentlandite (Fe$_{3.32}$Ni$_{6.68}$), 7) heazlewoodite (Fe$_{0.03}$Ni$_{2.97}$S$_{2.00}$) + violarite (Fe$_{2.20}$Ni$_{7.80}$) + $\gamma$ (Fe$_{2.03}$Ni$_{7.95}$), 8) and 9) pyrite (Fe$_{0.99}$Ni$_{0.01}$S$_{2.00}$) + vaesite (Fe$_{0.01}$Ni$_{0.99}$S$_{2.00}$) + monosulfide solid-solution (Fe$_{0.30}$Ni$_{0.50}$S$_{1.00}$) or S (liquid).

Violarite of composition Fe$_{0.70}$Ni$_{2.29}$S$_{4.00}$ (10.0 Fe, 32.8 Ni, 57.2 S at.% at 455°C) appears independently as a ternary phase within the S-rich portion of the system as a product of a peritectoid reaction between

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**Fig. 7.** The phase diagram in the Fe–Ni–S system at 470°C. See Table 1 for symbols: S(liq) : sulfur liquid.
monosulfide solid-solution (Fe_{0.32}Ni_{0.63}S_{1.00} at 460°C) and vaesite (Fe_{0.01}Ni_{0.99}S_{2.00} at 460°C) at 459° ± 3°C, as documented by microscopic examination and high-temperature X-ray powder diffraction. This phase grows as a limited solid-solution to the Ni-rich side by a pseudoperitectoid reaction between vaesite and monosulfide solid-solution with decreasing temperature. The Fe-rich end of the violarite series coexists with pyrite, vaesite and monosulfide solid-solution as two univariant assemblages of pyrite + vaesite + violarite and pyrite + monosulfide solid-solution + violarite at 459°C or below.

Phase relations at 450°C

Because of the disappearance of high-form pentlandite at 503°C and β, at 484°C, the phase relations at 450°C become simpler than those at 520° and 500°C, as seen in Figure 8. Monosulfide solid-solution still maintains a continuous field as before, but it becomes thinner. It coexists with pyrite, vaesite and violarite on the S-rich side and with pentlandite, high-form godlevskite, α and γ (Fe-rich) on the metal-rich side, but cannot coexist with heazlewoodite, awaruite and γ (Ni-rich) because of the stable tie-lines between pentlandite and high-form godlevskite. Pentlandite is also found as a principal phase as before, and it coexists with monosulfide solid-solution, high-form godlevskite, heazlewoodite and γ, but does not associate with pyrite, vaesite, violarite, α, awaruite and Ni-rich γ. It forms an elongate solid-solution of compositional range from Fe_{5.73}Ni_{3.27}S_{7.92} to Fe_{2.84}Ni_{6.16}S_{7.89}, including Fe_{4.5}Ni_{4.5}S_{8.0}, but becomes thinner than that at 500°C. We recognize seven univariant assemblages as follows: 1) monosulfide solid-solution (Fe_{0.99}Ni_{0.01}S_{1.00}) + α (Fe_{9.41}Ni_{0.59}) + γ (Fe_{6.42}Ni_{3.58}), 2) monosulfide solid-solution (Fe_{0.95}Ni_{0.03}S_{1.00}) + pentlandite (Fe_{5.73}Ni_{3.27}S_{7.92}) + γ (Fe_{4.55}Ni_{5.45}), 3) pentlandite (Fe_{2.84}Ni_{6.16}S_{7.89}) + monosulfide solid-solution (Fe_{0.13}Ni_{0.86}S_{1.00}) + high-form godlevskite (Fe_{0.05}Ni_{6.94}S_{6.00}), 4) pentlandite (Fe_{2.84}Ni_{6.16}S_{7.89}) + high-form godlevskite (Fe_{0.05}Ni_{6.94}S_{6.00}) + heazlewoodite (Fe_{0.02}Ni_{2.95}S_{2.00}), 5) pentlandite (Fe_{3.6}Ni_{3.5}S_{7.73}) + heazlewoodite (Fe_{0.04}Ni_{2.97}S_{2.00}) + γ (Fe_{4.17}Ni_{5.83}), 6) heazlewoodite (Fe_{0.02}Ni_{2.97}S_{2.00}) + γ (Fe_{4.08}Ni_{5.92}) + awaruite (Fe_{3.43}Ni_{6.57}), and 7) heazlewoodite (Fe_{0.02}Ni_{6.00}S_{2.00}) + awaruite (Fe_{2.11}Ni_{7.89}) + γ (Fe_{1.88}Ni_{8.12}) in the metal-rich portion of the isotherm at 450°C. On the other hand, violarite, which appeared at 459°C as above, grows as a limited solid-solution from Fe_{0.64}Ni_{2.37}S_{4.00} to Fe_{0.71}Ni_{2.20}S_{4.00} at 450°C. There are four more univariant assemblages in the S-rich portion of the system: 8) pyrite (Fe_{0.99}Ni_{0.01}S_{2.00}) + violarite (Fe_{0.71}Ni_{2.20}S_{4.00}) + vaesite (Fe_{0.02}Ni_{0.99}S_{2.00}), 9) pyrite (Fe_{0.99}Ni_{0.01}S_{2.00}) + vaesite (Fe_{0.02}Ni_{0.99}S_{2.00}) +
violarite (Fe$_{0.71}$Ni$_{0.29}$S$_{4.00}$) + monosulfide solid-solution (Fe$_{0.27}$Ni$_{0.65}$S$_{1.00}$) and 10) vaesite (Fe$_{0.01}$Ni$_{0.99}$S$_{2.00}$) + violarite (Fe$_{0.64}$Ni$_{0.37}$S$_{4.00}$) + monosulfide solid-solution (Fe$_{0.23}$Ni$_{0.72}$S$_{1.00}$) or 11) S (liquid). A limited solid-solution of violarite coexists with vaesite, pyrite and monosulfide solid-solution, and forms two univariant assemblages, 8 and 9) on the Fe-rich side, and a univariant assemblage, 10), on the Ni-rich side. Note the coexistence of pentlandite and awaruite found at 450°C; pentlandite appears in association with awaruite or γ (or both) below 431° ± 3°C, however.

**Phase Relations of the Fe$_{4.5}$Ni$_{4.5}$–S and Fe$_{0.9}$S–Ni$_{3}$S$_{2}$ Joins in the System Fe–Ni–S**

*Phase relations along the Fe$_{4.5}$Ni$_{4.5}$–S join*

The phase relations were investigated along the pseudobinary Fe$_{4.5}$Ni$_{4.5}$–S join at temperatures from 650° to 450°C using the evacuated silica-tube method, with a particular focus on a limited compositional range from 35 to 57 at.% S in order to unravel the thermal stability ranges of high- and low-form pentlandites coexisting with monosulfide solid-solution and γ. The experimental products were documented with optical microscopy, DTA, high-temperature X-ray diffraction and EPMA.

The resulting phase-diagram is shown in Figure 9. From the diagram, it is understood that high-form pentlandite transforms into pentlandite (low form) on cooling.

Pentlandite (low form), of composition Fe$_{4.5}$Ni$_{4.5}$S$_{8.0}$, is cubic Fm3m with an a parameter of 10.100 Å at room temperature. On the other hand, high-form pentlandite (Fe$_{4.5}$Ni$_{4.5}$S$_{7.95}$) is cubic Pn3m with an a of 5.194 Å at 650°C, corresponding to one half of the cell edge of pentlandite. This high–low inversion is reversible. It is considered to be a transition of an order–disorder type from the supercell (low form) to the subcell (Sugaki & Kitakaze 1992, 1998).

A portion of the high-form solid-solution containing less than 46 at.% S cannot invert into the low form, but successively exsolves pentlandite from the solid solution along a solvus, reducing its solid-solution field with decreasing temperature. Finally, the high-form solid-solution gets to composition Fe$_{4.5}$Ni$_{4.5}$S$_{7.36}$ (44.98 atomic % S) at 587° ± 3°C, corresponding to the end of the exsolution and the beginning of the pseudoeutectoid

![Figure 9](image_url)

**Fig. 9.** The phase relations of the Fe$_{4.5}$Ni$_{4.5}$–S join in the composition range from 35 to 60 at.% S at temperatures from 650° to 450°C in the Fe–Ni–S system. See Table 1 for symbols.
of the high form on the join. It breaks down into a mixture (univariant assemblage) of high-form pentlandite with a composition very slightly richer in Ni, pentlandite and \( \gamma \) at 587°C, and changes successively to the divariant assemblage pentlandite and \( \gamma \) at 585° ± 3°C upon cooling. The appearance of this univariant assemblage was ascertained as a narrow field over a limited range in temperature of only a few degrees such as 1°, 2°, 3° and 6° at 45.8, 45.0, 44.4 and 36.0 at.% S, respectively. In the portion richer in S than 47 at.% S as a bulk composition along the join, high-form pentlandite or pentlandite appear as the divariant assemblages with monosulfide solid-solution. These pentlandites experience a phase transition of the non mass-transfer type. In these cases, their inversion temperatures fall slightly from 615° to 611° ± 3°C with increasing S content of the bulk composition because a composition of pentlandite in the divariant assemblages becomes more Ni-rich than Fe = Ni in atomic %, so as to be off the join (Fig. 9).

**Phase relations along the Fe\( _{0.9} \)S–Ni\( _{3} \)S\(_{2} \) join**

We considered a pseudobinary phase-diagram for the join Fe\( _{0.9} \)S–Ni\( _{3} \)S\(_{2} \) (0 to 60 at.% Ni), passing through the ideal composition Fe\(_{4.5}\)Ni\(_{4.5}\)S\(_{8.0} \) of pentlandite in the system at temperatures from 650° to 450°C in order to examine the thermal stabilities of both high- and low-form pentlandite solid-solutions, and to ascertain their intricate relations with coexisting phases such as monosulfide solid-solution, \( \beta_1 \), high-form godlevskite and heazlewoodite below 600°C (Fig. 10). This figure corresponds to that at the same position as a cross section shown by Kullerud (1962, 1963a), but the phase relations in this diagram differ significantly from those shown by him because of the appearance of high-form pentlandite and \( \beta_1 \) as new phases, their eutectoids and the tie-line changes among the phases, as mentioned above. The phase relations are especially complicated in the Ni-rich portions below 550°C.

The high-form pentlandite solid-solution has a large wedge-like field, and coexists with monosulfide solid-solution, pentlandite or \( \beta_1 \) as the divariant assemblages in the join. On the other hand, pentlandite appears as limited solid-solution from 26.5 to 31.6 at.% Ni (561°C) below 614°C on the join and coexists with monosulfide solid-solution, high-form pentlandite, \( \beta_1 \), high-form godlevskite, and heazlewoodite or \( \gamma \) (or both) as the divariant and univariant assemblages. This pentlandite solid-solution mainly results from the phase transition from the high-form solid-solution on cooling. This

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**Fig. 10.** The phase relations in the Fe\( _{0.9} \)S–Ni\( _{3} \)S\(_{2} \) join of the system Fe–Ni–S at the temperatures from 650° to 450°C in the composition from 0 to 60 at.% Ni. See Table 1 for symbols. At 512°C, the tie-line changes between high-form pentlandite + heazlewoodite (high temperature) and high-form godlevskite + \( \beta_1 \) (low temperature) (see inset).
phase transition begins from high-form pentlandite with Fe$_{4.42}$Ni$_{14.58}$S$_{7.96}$ (27.0 at.% Ni) at 614°C as a non-mass-transfer inversion, continues as a mass-transfer inversion immediately and ends at 561°C and 31.6 at.% Ni of pentlandite. The field of the high-form solid-solution also decreases by exsolution along its solvus for pentlandite in addition to the phase transition with decreasing temperatures down to 561°C. At this temperature, the high-form pentlandite solid-solution of a composition with 40.0 atomic % Ni breaks down by a pseudoeutectoid reaction into a mixture of high-form pentlandite with a composition slightly poorer in S, pentlandite and $\beta_1$ as a univariant assemblage. However, high-form pentlandite of this univariant assemblage decreases in amount with decreasing temperature and disappears at 529°C, 40 at.% Ni. Its field changes to the divariant assemblage of pentlandite and $\beta_1$ below this temperature. High-form pentlandite (Fe-bearing $\beta_2$) is stable down to 503°C of its eutectoid in the system, but the fields of the univariant assemblage high-form pentlandite + pentlandite + $\beta_1$ disappear at a higher temperature (540°C to 509°C) than 503°C because those are off the join. The divariant assemblage high-form pentlandite + $\beta_1$ also disappears at 509°C.

Phase $\beta_1$ appears as a limited solid-solution with a compositional range from 60.0 at.% Ni on the Ni–S boundary of the system to 51.0 at.% Ni above 565°C on the join and coexists with high-form pentlandite. This phase, however, departs from the Ni–S boundary below this temperature owing to the appearance of heazlewoodite, and reduces abruptly its field with decreasing temperature and disappears at 507°C because the $\beta_1$ field actually lies off the join. But $\beta_1$ is stable down to 484°C of its eutectoid in the system, and appears extensively as the divariant and univariant assemblages with pentlandite, high-form godlevskite, and heazlewoodite or $\gamma$ (or both) at temperatures from 565°C to 484°C, as seen in the phase diagram (Fig. 10).

Heazlewoodite with Ni$_3$S$_2$ on the join first appears as a stable principal phase owing to the phase transition of $\beta_1$ at 565°C, and coexists with $\beta_1$ (565° to 484°C), high-form pentlandite (565° to 512°C), high-form godlevskite (524° to 397°C), pentlandite (below 498°C) and $\gamma$ (below 484°C) as the divariant and univariant assemblages in the join. Among them, the assemblage of pentlandite and heazlewoodite occurs as a principal association because of the tie-line change at 498°C or below, as already illustrated, in some cases in association with $\beta_1$, high-form godlevskite or $\gamma$. The univariant assemblage pentlandite, heazlewoodite and $\beta_1$ among them only appears at limited range in temperature, between 498° and 484°C. The univariant assemblages of pentlandite, heazlewoodite and high-form godlevskite or $\gamma$ is stable below 498° or 484°C, respectively. As mentioned above, the phase relations in the Ni-rich portion of the join below 550°C are complicated because of the occurrence of two tie-line changes, at 512° and 498°C, and two eutectoids of high-form pentlandite and $\beta_1$, at 503° and 484°C, respectively. An enlarged figure of that portion is given as an inset (Fig. 10).

Eutectoids of High-Form Pentlandite and $\beta_1$ Solid Solutions

High-form pentlandite solid-solution

The curves de and ei in Figure 11 correspond to a locus of the Fe-rich extremity of high-form pentlandite (Fe$_{5.60}$Ni$_{13.40}$S$_{7.82}$ at 625°C) at temperatures from 617° to 503°C (Fe$_{1.04}$Ni$_{7.96}$S$_{6.93}$). The Fe-rich curve show a “rapid” retreat of high-form pentlandite toward the Ni-rich side owing to a breakdown by two pseudoeutectoid reactions of the Fe-rich extremity of high-form pentlandite to the univariant assemblages high-form pentlandite with a slightly Ni-enriched composition + pentlandite + $\gamma$ at temperatures from 617° to 579°C and high-form pentlandite + pentlandite + $\beta_1$ at temperatures from 579° to 503°C with decreasing temperature, as already illustrated above. In addition to this, there are also found two other paths (the S- and Ni-rich paths) indicated as the curves fi and gi, respectively, in Figure 11. The former (S-rich curve) as the curve fi corresponds to a pseudoeutectoid reaction of high-form pentlandite breaking down to a mixture of high-form pentlandite with a slightly Ni-rich and S-poor composition + pentlandite (Ni-rich extremity) + high-form godlevskite (Fe-rich extremity) at temperatures from 568° to 503°C. The latter (Ni-rich path gi) consists of two pseudoeutectoid reactions decomposing to the univariant assemblages high-form pentlandite (Fe-free and Fe-bearing $\beta_2$) + high-form godlevskite + heazlewoodite at temperatures from 524° to 512°C as the curve gh and high-form pentlandite + high-form godlevskite + $\beta_1$ at temperatures from 512° to 503°C as the curve hi (Fig. 11).

These courses of the pseudoeutectoid reactions reach a ternary eutectoid (i) of high-form pentlandite at 503°C and Fe$_{1.04}$Ni$_{7.96}$S$_{6.93}$ (6.5Fe, 50.0Ni, 43.5S in at.%). Thus, high-form pentlandite (Fe-bearing $\beta_2$) finally breaks down to a mixture of pentlandite (Fe$_{2.44}$Ni$_{6.56}$S$_{7.85}$), high-form godlevskite (Fe$_{0.40}$Ni$_{6.61}$S$_{6.00}$) and $\beta_1$ (Fe$_{0.20}$Ni$_{2.62}$S$_{2.00}$), and disappears below this temperature.

In addition to these pseudoeutectoid reactions, exsolution of the high-form pentlandite solid-solution occurs in the metal-rich (S-poor) boundaries of pentlandite (625° to 503°C) and high-form godlevskite (568° to 503°C), and in S-rich $\beta_1$ (above 650° to 503°C) and heazlewoodite (564° to 512°C) (Fig. 11).

The $\beta_1$ solid-solution

Phase $\beta_1$ also reduces its field with decreasing temperature. In this case, we document four paths of the pseudoeutectoid reactions of the $\beta_1$ solid-solution...
along the Fe, Ni and S-rich and intermediate courses as shown in Figure 11. Among them, the Fe-rich path consists of two pseudoeutectoid reactions breaking down the Fe-rich extremity of $\beta_1$ solid solution to the mixtures (univariant assemblages) of $\beta_1$ with a slightly Ni-rich composition + high-form pentlandite + $\gamma$ at temperatures from above 650°C (~700°C) to 579°C as a curve $jk$ (Fig. 11) and $\beta_1$ + pentlandite + $\gamma$ at temperatures from 579° to 484°C (eutectoid of $\beta_1$) as a curve $kq$ (Fig. 11), successively.

Along the S-rich path, the S-rich $\beta_1$ solid-solution breaks down to the univariant assemblage of $\beta_1$ (Fe-free to a slightly Fe-bearing composition) + high-form godlevskite $\beta_1$ at 512°C and a point $i$ (564°C, 40.6 at.% S) with decreasing temperature. After a tie-line change from high-form pentlandite + heazlewoodite to high-form godlevskite $\beta_1$ at 512°C and a point $m$ (Fig. 11), the path of the pseudoeutectoid reaction changes suddenly to the S-poor direction for the eutectoid, a point $q$ of the $\beta_1$ solid-solution. In this case, the course divides into two routes, two $mn$ and $no$ curves due to the disappearance of high-form pentlandite at 503°C, and a curve $mo$ from 512° to 498°C, at which point the tie-line change from high-form godlevskite $\beta_1$ to pentlandite + heazlewoodite. We have found three pseudoeutectoid reactions of the $\beta_1$ solid-solution as follows: breakdowns of $\beta_1$ to 1) a mixture of $\beta_1$ with a slightly S-poor and Fe-rich composition + high-form pentlandite + high-form godlevskite from 512° to 503°C along a curve $mn$, 2) a mixture of $\beta_1$ + pentlandite + high-form godlevskite from 503° to 498°C along a curve $no$, and 3) a univariant assemblage of $\beta_1$ + high-form godlevskite + heazlewoodite from 512° to 498°C along a curve $mo$. After the tie-line change from high-form godlevskite $\beta_1$ to pentlandite + heazlewoodite at 498°C, $\beta_1$ further breaks down to a univariant assemblage of $\beta_1$ + pentlandite + heazlewoodite as the pseudoeutectoid reaction along a curve $oq$ (Fig. 11) from 498° to 484°C.

As shown in Figure 11, a curve $kn$ branches off at 579°C and a point $k$ from the path $jq$ appears as another pseudoeutectoid reaction of the $\beta_1$ solid-solution breaking down to a mixture of $\beta_1$ with a slightly Ni- and S-rich composition + high-form pentlandite + pentlandite as the intermediate path, and joins a point $n$ (Fe$_{0.20}$Ni$_{2.67}$S$_{2.00}$) at 503°C. After that, $\beta_1$ decreases its amount of S via the curves $no$ and $oq$ as the two pseudoeutectoid reactions with decreasing temperature, and leads to the eutectoid $q$ (484°C), as already illustrated above.

The pseudoeutectoid breakdown of $\beta_1$ is also observed as a Ni-rich path along a simple curve, $pq$. Its breakdown product is a mixture of $\beta_1$ with a slightly Fe-bearing composition + heazlewoodite + $\gamma$ continuously at temperatures from 533° to 484°C.
Exsolution of the $\beta_1$ solid-solution from high-form pentlandite, pentlandite, high-form godlevskite, heazlewoodite and $\gamma$, in addition to the pseudoeutectoid reactions of $\beta_1$ mentioned above, also reduce its field with decreasing temperature. Concretely, exsolution of the $\beta_1$ solid-solution occurs by a reduction of the field in those compositions richer in S than those along the curves $jk$, $kn$, $nm$ and $ml$ from above $650^\circ$ ($\sim 700^\circ$) to $503^\circ$ for the metal-rich (S-poor) boundary of the high-form pentlandite, an area enclosed by the curves $kn$, $no$, $oq$, and $kq$ from $579^\circ$ to $484^\circ$ for the metal-rich boundary of pentlandite, a small field surrounded by the curves $mn$, $no$ and $mo$ (Ni-rich side) from $512^\circ$ to $498^\circ$C for high-form godlevskite, an area enclosed by the curves $lm$, $mo$ (Ni-rich side), $oq$ and $pq$ from $564^\circ$ to $484^\circ$C for heazlewoodite, and a field with compositions poorer in S and richer in metal than those of the curves of $jk$, $kq$ and $pq$ from above $650^\circ$ ($\sim 700^\circ$) to $484^\circ$C for $\gamma$.

Finally, $\beta_1$ breaks down to a mixture of pentlandite ($Fe_{3.23}Ni_{3.77}S_{7.79}$) + heazlewoodite ($Fe_{0.11}Ni_{3.90}S_{2.00}$) + $\gamma$ ($Fe_{3.98}Ni_{6.51}$) at a ternary eutectoid, $484^\circ$ + $3^\circ$ and $Fe_{0.26}Ni_{2.57}S_{2.00}$, and disappears below this temperature. The phase $\beta_1$ is unable to coexist with monosulfide solid-solution and awaruite because of the stable tie-lines between pentlandite and high-form godlevskite and between heazlewoodite and $\gamma$, respectively.

**Discussion and Summary**

*High-low inversion of pentlandite*

Kullerud (1962, 1963a) carried out experiments to document the thermal stability of pentlandite ($Fe_{4.5}Ni_{4.5}S_{8.0}$) by means of DTA and a high-temperature X-ray powder-diffraction camera. He found a very strong thermal effect as a first endothermic peak of the DTA curve at $610^\circ$C on heating, interpreted to be a breakdown of pentlandite and not its polymorphic inversion because the peak of the DTA at $610^\circ$C required a larger latent heat anomaly than that of a second peak, involving melting at $863^\circ$C. The latent heat anomaly of the phase transition of sulfide minerals is in general thought to be smaller than that of their breakdown or melting. Such a large latent heat of pentlandite is a rare case at an inversion of sulfide. Sugaki & Kitakaze (1992, 1998) reported that this is caused by a peculiarity in the crystal structure of pentlandite, which is characterized by an alternation in the arrangement of subcells, with eight tetrahedrally coordinated cations and with an octahedrally coordinated cation (Lindqvist et al. 1936, Rajamani & Prewitt 1973). Such a transformation from a distinctively ordered structure into a disordered primitive cubic cell is considered to cause a large heat anomaly in the case of pentlandite.

An X-ray powder-diffraction pattern of high-form pentlandite resembles that of phase Ni$_{3a_x}$S$_2$ (high-form heazlewoodite). Therefore, it is a possibility that high-form pentlandite was misidentified with phase Ni$_{3a_x}$S$_2$ by Kullerud (1962, 1963a).

The high-low inversion between high-form pentlandite and pentlandite was first found by Sugaki & Kitakaze (1992, 1998). They reported that a euhedral crystal of high-form pentlandite synthesized by the vapor-transport and flux methods at $770^\circ$ and $800^\circ$C, respectively, transforms to pentlandite (low form) at $600^\circ$ and $25^\circ$C reversibly in a representative 110 precession photograph for a single crystal with a composition, for example, $Fe_{4.5}Ni_{4.5}S_{7.95}$. This fact was furthermore ascertained by using the high-temperature X-ray powder diffraction, DTA and EPMA (BSE) for both the high- and low-form pentlandites synthesized by the evacuated silica-glass-tube method (Sugaki & Kitakaze 1998, this study).

High-form pentlandite has a large solid-solution field at $650^\circ$C (Fig. 2) in this study. However, the area of its field is smaller than that of the (Ni,Fe)$_{3a_x}$S$_2$ solid-solution at $725^\circ$C found by Karup-Møller & Makovicky (1995) because our high-form field does not include a $\beta_1$ field. High-form pentlandite reduces its field rapidly owing to the phase transition and exsolution of pentlandite and breaks down by pseudoeutectoid and pseudoperitectoid reactions with decreasing temperatures below $625^\circ$C, where the high-low inversion of pentlandite begins as illustrated above. Finally, high-form pentlandite breaks down to a mixture of pentlandite, high-form godlevskite and $\beta_1$ at a ternary eutectoid, $503^\circ$C and $Fe_{1.04}Ni_{7.96}S_{6.93}$, and disappears completely below this temperature in the system.

*High-form pentlandite solid-solution*

No phase corresponding to high-form pentlandite solid-solution, including $Fe_{4.5}Ni_{4.5}S_{8.0}$, was found at temperatures above $610^\circ$C by Kullerud (1963a, 1963b), Kullerud *et al.* (1969) and Craig & Kullerud (1969), although they reported the appearance of Ni-rich ternary phase (Ni,Fe)$_{3a_x}$S$_2$ at $862^\circ$C whose solid-solution field approached the Ni–S boundary with decreasing temperature. Hsieh *et al.* (1982) also showed the existence of a $\beta$ solid-solution as a small lenticular field of a ternary composition near a liquid field at $850^\circ$C. Their $\beta$ phase has more Ni-rich and S-poor compositions than $Fe_{4.5}Ni_{4.5}S_8$, but is located within a field of liquid or near its S-rich boundary in the isotherm at $850^\circ$C by Sugaki & Kitakaze (1998). Sugaki *et al.* (1983, 1984) found an extensive field of high-form pentlandite from more Fe-rich compositions than $Fe_{4.5}Ni_{4.5}S_{8.0}$ to Ni$_{3a_x}$S$_2$ of the Ni–S boundary at $800^\circ$ and $650^\circ$C. Hayashi (1985) also recognized the existence of this same solid-solution in the equilibrium experiments within the quaternary system Cu–Fe–Ni–S at $800^\circ$, $650^\circ$ and $600^\circ$C. Fedorova & Sinyakova (1993) investigated the isothermal phase relations in the Fe–Ni–S system at $900^\circ$, $820^\circ$ and $600^\circ$, and reported an extended...
heazlewoodite solid-solution ($\text{Fe}_2\text{Ni}_{1-x}\text{S}_2$) at 820° and 600°C. Karup-Møller & Makovicky (1995) also showed an elongate field of ($\text{Ni}_3\text{Fe}_{3-x}$)$_{3\text{S}_2}$ projected from the Ni–S boundary in their phase diagram at 725°C. Both of the solid solutions by these authors correspond to the high-form pentlandite $\text{Ni}_{3\text{S}_2}$ solid-solution of Sugaki et al. (1984).

Note that $\text{Ni}_{3\text{S}_2}$ is not a single phase, but consists of $\beta_1$ and $\beta_2$ phases, as already mentioned (Lin et al. 1978, Sharma & Chang 1980, Singleton et al. 1991, Kitakaze & Sugaki 1996, 2001). Therefore, it is important to elucidate whether or not $\beta_1$ or $\beta_2$ could coexist with the high-form pentlandite solid-solution. As a result, it was proved that the high-form pentlandite solid-solution and $\beta_2$ form a continuous solid-solution at 806°C and below (Sugaki & Kitakaze 1996). This is to be expected because the unit-cell type, cell edge and metal:S ratio in the composition of $\beta_2$, in comparison with $\beta_1$, are more similar to those of high-form pentlandite, where Fe = Ni. This high-form pentlandite $\beta_2$ solid-solution is maintained at temperatures from 806° to 503°C. Phase $\beta_1$ appears as an independent phase with a limited solid-solution field projecting into the ternary system from the Ni–S boundary below 800°C, and coexists stably with the high-form pentlandite solid-solution. However, the high-form pentlandite solid-solution, such as high-form pentlandite $\text{Ni}_{3\text{S}_2}$ solid-solution at 650°C of Sugaki et al. (1984) and Hayashi (1985), heazlewoodite solid-solution at 600°C of Fedorova & Sinyakova (1993) and (Ni,Fe)$_{3\text{S}_2}$ at 725°C of Karup-Møller & Makovicky (1995), include the $\beta_1$ composition and lie outside of the composition of $\beta_2$. Consequently, these solid-solutions are not monophases, and the phase assemblages and compositional ranges in the Ni-rich portion of the solid solutions obtained by these authors differ from those in the present study. For example, an odd form of the heazlewoodite (high-form pentlandite) solid-solution in the diagram at 600°C of Fedorova & Sinyakova (1993) may be a consequence of the inclusion of $\beta_1$ within the solid-solution field. However, their interpretation of phase relations at 820°C, for which no $\beta_1$ and $\beta_2$ appear, are similar to those at 850°C obtained by Sugaki & Kitakaze (1998), although our solid solution and liquid have more S-rich compositions than those of Fedorova & Sinyakova (1993). Recently, Sack & Ebel (2006) commented that the experimental results by Sugaki & Kitakaze (1998) for high-form pentlandite are consistent with those of Fedorova & Sinyakova (1993) and Karup-Møller & Makovicky (1995).

Kitakaze & Sugaki (2004) showed a field of the Co-free high-form pentlandite solid-solution on a Fe–Ni–S face of a tetrahedron of the system Fe–Ni–Co–S at 650°C. However, it was incorrectly stated that all the S-rich extreme compositions of the high-form pentlandite solid-solution were poorer in S than Fe$_{3\text{Ni}_{1-x}}$S$_8$ ($x = 5.5$ to 0.2, 47.06 at.% S) at 650°C. As a result of re-examination in this study, it was ascertained that the S-rich extreme compositions of the high-form pentlandite solid-solution in the portion richer in Fe than the Fe$_3\text{Ni}_{1-x}$–S join are approximately 47.1 at.% S, except for around the Fe-rich end (Fe$_{5.65}\text{Ni}_{3.35}$S$_{7.82}$; 33.6 Fe, 19.9 Ni, 46.5 S in at.% S) of high-form pentlandite extended to the more Fe-rich side (Fig. 4). Those of the portion richer in Ni than $x = 3.30$ of Fe$_{3\text{Ni}_{1-x}}$–S join became poorer in S than 47.06 at.% S, such as Fe$_{3.50}\text{Ni}_{5.50}$S$_{7.98}$ (47.00 at.% S), Fe$_{3.0}\text{Ni}_{6.0}$S$_{7.95}$ (46.90 at.% S), Fe$_{2.9}\text{Ni}_{6.1}$S$_{7.92}$ (46.81 at.% S) and Fe$_{2.2}\text{Ni}_{6.5}$S$_{7.85}$ (46.59 at.% S) with increasing Ni content.

High-form pentlandite (Fe-bearing $\beta_2$) of a composition very close to Fe$_{1.04}\text{Ni}_{1.96}$S$_{6.93}$ at 505°C finally breaks down to a mixture of pentlandite, $\beta_1$ and high-form godlevskite in a eutectoid reaction at 503° ± 3°C. This temperature is approximately similar to that of the heazlewoode solid-solution found by Fedorova & Sinyakova (1993), although the reaction is more complicated in their phase diagram because the solid-solution encloses $\beta_1$.

According to Fedorova & Sinyakova (1993), the univariant assemblage monosulfide solid-solution + Fe-rich heazlewoodite (high-form pentlandite) solid-solution + Fe-rich pentlandite is stable at 600°C. However, no such univariant assemblage was found in our study at 617°C or below because the tie-lines between the Fe-rich extremity of pentlandite and $\gamma$ are stable instead of the tie-lines between monosulfide solid-solution and high-form pentlandite below this temperature.

Because of the appearance of high-form pentlandite, nine univariant assemblages are established as follows: 1) high-form pentlandite + monosulfide solid-solution + $\gamma$ (above 650° to 617°C), 2) high-form pentlandite + pentlandite + $\gamma$ (617° to 579°C), 3) pentlandite + high-form pentlandite + $\beta_1$ (579° to 503°C), 4) high-form pentlandite + $\beta_1$ + $\gamma$ (above 650° to 579°C), 5) monosulfide solid-solution + pentlandite + high-form pentlandite (603° to 568°C), 6) high-form pentlandite + pentlandite + high-form godlevskite (568° to 503°C), 7) high-form pentlandite + high-form godlevskite + heazlewoodite (524° to 512°C), 8) high-form pentlandite + $\beta_1$ + heazlewoodite (564° to 512°C), and 9) high-form pentlandite + high-form godlevskite + $\beta_1$ (512° to 503°C) (Fig. 11). Among them, the four univariant assemblages (3, 4, 8 and 9) coexisting with $\beta_1$ are new ones not found in the previous literature.

**Pentlandite**

The compositional ranges of the pentlandite solid-solutions at temperatures from 625° to 450°C in this study are shown in comparison with those obtained by Shewman & Clark (1970), Misra & Fleet (1973a, 1973b) and Ueno _et al._ (2000) in Figure 12. These solid-solution ranges overlap each other in a principal portion, except for both the Fe- and Ni-rich extremities.
of the solid solutions as seen in the figure. There also is roughly a tendency that the solid-solution range moves gradually to the Fe-richer side with decreasing temperature. A compositional range from Fe$_{5.68}$Ni$_{3.32}$S$_{7.85}$ to Fe$_{2.43}$Ni$_{6.57}$S$_{7.85}$ (46.59 at.% S) including Fe$_{4.5}$Ni$_{4.5}$S$_{8}$ at 500°C by us is approximately the same as those obtained by these authors except Shewman & Clark (1970). The pentlandite solid-solution retreats its Ni-rich extremity to the inside of the ternary so as to reduce its field below 500°C (Shewman & Clark 1970, Ueno et al. 2000, this study).

According to the previous papers (Kullerud 1963b, Naldrett et al. 1967, Kullerud et al. 1969, Shewman & Clark 1970, Fedorova & Sinyakova 1993), pentlandite cannot coexist with γ at temperatures from 575° to 600°C because the FeS–(Ni,Fe)$_{3±x}$S$_2$ tie-lines are stable. However, no such tie-lines were found in this study. Pentlandite can coexist with γ over a wide range of temperature, from 617° to 450°C or below. The assemblage of the most Ni-rich pentlandite and heazlewoodite as seen in Ni–Cu ores appears first at 498° ± 3°C by the tie-line change mentioned already. This is in good agreement with the estimate of approximately 500°C by Kullerud (1963b).

Pentlandite is also produced by exsolution from the high-form pentlandite and β$_1$ solid-solutions of ternary compositions with decreasing temperature and by those breakdowns at 503° and 484°C, respectively, at eutectoids, as already stated above.

Kitakaze & Sugaki (2004) reported that a single phase of pentlandite of compositions Fe$_{1.0}$Ni$_{6.0}$S$_{8.0}$ and Fe$_{2.5}$Ni$_{6.5}$S$_{8.0}$ undergoes a phase transition of non-mass-transfer type at 603° and 597° ± 3°C, respectively. That, however, was incorrect as results of the re-examinations by DTA at slow heating and cooling rates at 1° or 0.3/min and with high-temperature X-ray diffraction treated at 1° interval in detail in this study. That is, their non-mass-transfer inversion of pentlandite (Fe$_{3.0}$Ni$_{6.0}$S$_{7.85}$, 46.59 at.% S) at temperatures from 586° to 600°C and a pseudoperitectoid reaction for the Ni-rich extremity of pentlandite (Fe$_{3.0}$Ni$_{6.0}$S$_{7.87}$, 46.71 at.% S) at 594°C on the Fe$_{3.0}$Ni$_{6.0}$–S join in this study. On the other hand, the non-mass-transfer inversion of pentlandite (Fe$_{2.5}$Ni$_{6.5}$S$_{8.0}$) at 597°C of Kitakaze & Sugaki (2004) was found to be a reaction yielding pentlandite in the univariant assemblage as a bulk composition with 14.82 Fe, 38.53Ni and 46.65 S in at.% due to a pseudoperitectoid reaction between monosulfide solid-solution and high-form pentlandite at this temperature on the Fe$_{2.5}$Ni$_{6.5}$–S join upon cooling.

Bell et al. (1964) studied the physical stability of pentlandite by a high-pressure DTA method, and found that the breakdown temperature of synthetic pentlandite (Fe$_{4.5}$Ni$_{4.5}$S$_{8}$) into a mixture of pyrrhotite and high heazlewoodite (α) or low (β) heazlewoodite falls to 535°C at 14 kbar and 425°C at 25 kbar. However, these temperatures may correspond to those of the high–low
inversion of pentlandite. If so, the inversion temperatures of high- and low-form pentlandites may well decrease significantly with increasing pressure, but we have no such a data about its pressure effect.

**Genesis of pentlandite ore**

High-form pentlandite with Fe = Ni in at.% can crystallize from liquid at temperatures from 865° to 746°C in the system Fe–Ni–S (Sugaki & Kitakaze 1998). This implies that Ni–Cu sulfide ores with high-form pentlandite can form by crystallization from sulfide magma in a geological process, as supported by many published observations and descriptions in the previous literature (e.g., Lindgren 1933, 1937, Bateman 1952, Hawley 1962, Ramdohr 1980). From our experimental data and referring to previous papers on pentlandite genesis, we propose that pentlandite forms by the following genetic processes: 1) a phase transition (625° to 550°C in the Fe–Ni–S system) from high-form pentlandite crystallized primarily from sulfide magma by successive peritectic and eutectic (or pseudoperitectic or pseudo-eutectic) reactions (865° to 746°C for Fe = Ni in the Fe–Ni–S system) (Sugaki et al. 1983, 1984, Fedorova & Sinyakova 1993, Karup-Møller & Makovicky 1995, Sugaki & Kitakaze 1998, this study), 2) an exsolution from the S-rich extremity (boundary) of the high-form pentlandite solid-solution consuming its large field with decreasing temperatures, from 625° to 503°C for the metal-rich boundary of the pentlandite solid-solution, 3) an exsolution of the metal-rich boundary of monosulfide solid-solution below 625°C in the case of the S-rich extremity of the pentlandite solid-solution, appearing as a narrow rim of a portion richer in S (Edwards 1954, Hawley 1962, Naldrett et al. 1967, Francis et al. 1976, Ramdohr 1980, Craig & Vaughan 1981, Fedorova & Sinyakova 1993, this study), 4) an exsolution from a field of the β1 solid-solution enclosed by the curves kn, no, oq, and kq (Fig. 11) with falling temperatures from 579° to 484°C for the metal(Ni)-rich boundary of pentlandite, 5) a peritectoid relationship at 603°C and a pseudoperitectoid relationship from 603° to 568°C continuously between monosulfide solid-solution and high-form pentlandite for the growth of the Ni-rich extremity of pentlandite, with a composition richer in S (and Ni) than the curve bc (Fig. 11), 6) two pseudoperitectoids between monosulfide solid-solution and the Fe-rich extremity of high-form pentlandite at temperatures from 625° to 617°C and between monosulfide solid-solution and γ at temperatures from 617° to 450°C or below, successively, for minor growth of the Fe-rich extremity of pentlandite (Fedorova & Sinyakova 1993, this study), 7) two successive pseudoeutectoids of the Fe-rich extremity of high-form pentlandite breaking down to pentlandite with a metal-rich extreme composition (and γ or β1) at temperatures from 617° to 579°C as the curve de and from 579° to 503 as the curve ei, respectively (Fig. 11), 8) pseudoeutectoid of high-form pentlandite at temperatures from 568° to 503°C as the curve fi (Fig. 11) for the growth of the Ni-rich extremity of pentlandite successively from 5) pseudoperitectoid reaction, 9) pseudoeutectoid of monosulfide solid-solution at temperatures from 568° to 500°C for the Ni-rich end of pentlandite (and high-form godlevskite) and an exsolution from Fe-bearing high-form godlevskite below 503°C for the Ni-rich extremity of pentlandite, 10) a eutectoid of high-form pentlandite (Fe1.04Ni7.96S6.93) breaking down to the Ni-rich extremity of pentlandite, (high-form godlevskite and β1) at 503, (i in Fig. 11) and 11) a eutectoid of β1 (Fe0.26Ni2.68S2.00) breaking down to pentlandite, (heazlewoodite and γ) at 484°C (q in Fig. 11).

Among these possibilities, pentlandite in magmatic Ni–Cu sulfide deposits is considered to have been formed principally by the reactions of 1) to 5). Pentlandite can also appear as a product by hydrothermal precipitation and replacement below 600°C (e.g., Lindgren 1937, Bateman 1952, Edwards 1954, Hawley 1962, Park & MacDiarmid 1964, Sugaki & Kitakaze 1990). In his review, Fleet (2006) reported that high-form pentlandite (Fe = Ni) crystallizes from metal-rich liquid between 865° and 746°C, as described in a series of presentations extending from Sugaki et al. (1982) to Sugaki & Kitakaze (1998); he noted that pentlandite in magmatic sulfide ores in generally understood to form by segregation or phase separation from monosulfide solid-solution in the subsolidus.

Pentlandite from the magmatic Cu–Ni ore deposits commonly is associated with pyrrhotite and chalcopyrite, and in some cases, cubanite and bornite. Accordingly, to study the genesis of pentlandite ore, it is necessary to ascertain the phase relations in the quaternary system Fe–Ni–Cu–S in addition to those of the ternary Fe–Ni–S. For such a purpose, phase-equilibrium studies of the quaternary Fe–Ni–Cu–S in relation with the ore genesis of the Cu–Ni deposits have already been carried out by Craig & Kullerud (1969), Hill (1983) and Hayashi (1985). Although they reported the diveriant and univariant assemblages among the phases on the Fe–Ni–S, Cu–Ni–S, Cu–Fe–S and Cu–Fe–Ni faces of the quaternary tetrahedron, they found no four-component phase within the Cu–Fe–Ni–S tetrahedron except for a limited quaternary solid-solution increasing slightly within the tetrahedron from the Fe–Ni–S or Cu–Fe–S faces as monosulfide solid-solution, pentlandite and heazlewoodite or bornite and intermediate solid-solution, respectively.

Kitakaze (1998) found three sulfide phases, X [(Fe,Cu)6Ni5S8], Y [CuFe6Ni2S8] and Z [Cu2FeNi2S5], in the system Fe–Ni–Cu–S as unknown minor minerals in lherzolite of the Horoman peridotite massif in the southern mountains of Hidaka, Hokkaido, Japan. These phases were approved by the Committee for New Minerals and Mineral Names of the International
Mineralogical Association and named as sugakiite Cu(Ni,Fe)S₃S₈ for phase Y (Kitakaze 2008a), and horomanite (Fe,Ni,Co,Cu),S₈ and samanite Cu₁₋ₓFeₓS₂ (their terminology) in the quaternary system Fe–Ni–Cu–S at 760°C. These facts suggest a possibility that the phase relations in the quaternary system Fe–Ni–Cu–S will be more complicated than those presented by the authors of the literature previously cited here.

The phase equilibria in the system Fe–Ni–Co–S, especially on the Fe₀S₈–Ni₀S₈–Co₀S₈ plane in the tetrahedron, were investigated by Knop & Ibrahim (1961), Kojonen (1976) and Kaneda et al. (1986). These authors ascertained the existence of a complete solid-solution between (Ni,Fe)S₂ and intermediate solid-solution Cu₁₋ₓFeₓS₂ (their terminology) in the quaternary system Fe–Ni–Cu–S at 760°C. These facts suggest a possibility that the phase relations in the quaternary system Fe–Ni–Cu–S will be more complicated than those presented by the authors of the papers cited in the introduction.

The ore genesis of pentlandite should be considered in terms of the system Fe–Ni–Co–Cu–S. Therefore, more experimental data, especially about low-S-fugacity assemblages involving pentlandite, phase-equilibrium studies on the quaternary systems Fe–Ni–Cu–S and Fe–Ni–Cu–S, and finally the system Fe–Ni–Cu–S, will be needed.

ACKNOWLEDGEMENTS

We thank S.D. Scott, L.C. Hsu and an anonymous referee for critical reviews and valuable comments on this paper. The authors are grateful for assistance with the experiments by T. Hayashi. Expenses for this study were partially defrayed by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sport, Science and Technology of Japan, to which the authors offer their sincere thanks.

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Received June 10, 2009, revised manuscript accepted September 10, 2011.