

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, $\text{Fe}_{5.65}\text{Ni}_{3.35}\text{S}_{7.85}$, β_2 ($\text{Ni}_{4\pm x}\text{S}_3$), occurs in the system Fe–Ni–S at 650°C. This solid solution coexists with monosulfide solid-solution, β_1 ($\text{Ni,Fe}_{3\pm x}\text{S}_2$) and γ (Fe,Ni). Pentlandite with a composition $\text{Fe}_{5.60}\text{Ni}_{3.40}\text{S}_{7.82}$ 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 $\text{Fe}_{5.64}\text{Ni}_{3.36}\text{S}_{7.82}$ to $\text{Fe}_{3.25}\text{Ni}_{5.75}\text{S}_{7.92}$ at 600°C and from $\text{Fe}_{5.68}\text{Ni}_{3.32}\text{S}_{7.85}$ to $\text{Fe}_{2.43}\text{Ni}_{6.57}\text{S}_{7.85}$ 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 β_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), γ (below 617°C) and β_1 (579° to 484°C). High-form pentlandite still remains stable below 520°C, but breaks down to pentlandite, high-form godlevskite and β_1 at 503° ± 3°C and $\text{Fe}_{1.04}\text{Ni}_{7.96}\text{S}_{6.93}$ (eutectoid). Phase β_1 also breaks down to pentlandite, heazlewoodite and γ at 484° ± 3°C and $\text{Fe}_{0.26}\text{Ni}_{2.87}\text{S}_{2.00}$ (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 β_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 equilibria.

SOMMAIRE

La forme désordonnée de la solution solide pentlandite, $\text{Fe}_{5.65}\text{Ni}_{3.35}\text{S}_{7.85}$, β_2 ($\text{Ni}_{4\pm x}\text{S}_3$), occupe un champ de stabilité allongé dans le système Fe–Ni–S à 650°C. Cette solution solide coexiste avec une solution solide monosulfurée, β_1 ($\text{Ni,Fe}_{3\pm x}\text{S}_2$) et γ (Fe,Ni). La pentlandite ayant une composition $\text{Fe}_{5.60}\text{Ni}_{3.40}\text{S}_{7.82}$ 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 $\text{Fe}_{5.64}\text{Ni}_{3.36}\text{S}_{7.82}$ à $\text{Fe}_{3.25}\text{Ni}_{5.75}\text{S}_{7.92}$ à 600°C et de $\text{Fe}_{5.68}\text{Ni}_{3.32}\text{S}_{7.85}$ à $\text{Fe}_{2.43}\text{Ni}_{6.57}\text{S}_{7.85}$ à 500°C en réponse à des transitions de phases continues, l'exsolution et la déstabilisation par relations pseudopéritectoides et pseudo-eutectoides affectant la solution solide désordonnée, et l'exsolution et la déstabilisation (pseudo-eutectoides) de β_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), γ (en dessous de 617°C) et β_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 β_1 à 503° ± 3°C et $\text{Fe}_{1.04}\text{Ni}_{7.96}\text{S}_{6.93}$ (eutectoides). La phase β_1 aussi se déstabilise pour donner pentlandite, heazlewoodite et γ à 484° ± 3°C et $\text{Fe}_{0.26}\text{Ni}_{2.87}\text{S}_{2.00}$ (eutectoides). 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 minerais 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 et relations eutectoides impliquant la pentlandite désordonnée (solution solide), la solution solide monosulfurée et β_1 . 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° et 750°C.

(Traduit par la Rédaction)

Mots-clés: système Fe–Ni–S, pentlandite, godlevskite, solution solide monosulfurée.

INTRODUCTION

Since the study by Kullerud (1962, 1963a), it has been accepted that pentlandite ($\text{Fe}_{4.5}\text{Ni}_{4.5}\text{S}_8$) breaks down to a mixture of pyrrhotite (monosulfide solid-solution) and phase $\text{Ni}_{3\pm x}\text{S}_2$ at $610^\circ \pm 3^\circ\text{C}$ 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 $\text{Fe}_{4.5}\text{Ni}_{4.5}\text{S}_{7.9}$ does not break down but transforms into a high form at $615^\circ \pm 3^\circ\text{C}$, and that a continuous solid-solution between this high form and phase $\text{Ni}_{3\pm x}\text{S}_2$ is stable in the system Fe–Ni–S at 800° and 650°C (Sugaki *et al.* 1982, 1984). Fedorova & Sinyakova (1993) reported an extended heazlewoodite solid-solution ($\text{Fe}_x\text{Ni}_{1-x}\text{S}_{2+y}$) at 820° and 600°C in the system Fe–Ni–S. Also, Karup-Møller & Makovicky (1995) ascertained the existence of an elongate solid-solution with composition $(\text{Ni},\text{Fe})_{3\pm x}\text{S}_2$ 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–NiS–Ni phase diagram and recognized pentlandite, monosulfide solid-solution, heazlewoodite solid-solution and metal phases. But β_1 and β_2 in the binary system Ni–S described below were not found, so some problem has remained. Furthermore, Hayashi (1985) recognized the existence of a $(\text{Fe},\text{Ni})_9\text{S}_8\text{--Ni}_{3\pm x}\text{S}_2$ solid solution in his study of the quaternary system Cu–Fe–Ni–S at 850° 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 $(\text{Ni},\text{Fe})_{3\pm x}\text{S}_2$ and intermediate solid-solution $\text{Cu}_{1\pm x}\text{Fe}_{1\pm y}\text{S}_2$ 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 $\text{Ni}_{3\pm x}\text{S}_2$ (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 β_1 (Ni_3S_2 corresponding to a high form of heazlewoodite) and β_2 (Ni_4S_3 , a high-temperature phase), with a narrow field of immiscibility between them over the temperature range from 524° to 806°C. Accordingly, the high-form pentlandite, $\text{Ni}_{3\pm x}\text{S}_2$ solid-solution mentioned above

must be incorrect as it is possible for high-form pentlandite to form a continuous solid-solution with either β_1 or β_2 , but not both.

The appearance of high-form pentlandite, β_1 and β_2 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, β_1 and β_2 and their thermal stabilities, we have investigated seven isotherms in the system Fe–Ni–S at 10° to 20° intervals from 650° to 450°C, especially where both high or low pentlandite (or both) and β_1 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°, 600°, 550°, 520°, 500°, 470° 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° 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 ($\alpha\text{-Ni}_7\text{S}_6$; 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, β_1 and β_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., $\text{Fe}_{5.6}\text{Ni}_{3.3}\text{S}_{7.85}$ and $\text{Fe}_{5.2}\text{Ni}_{3.7}\text{S}_{8.05}$) 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° 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 β_1 and β_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° 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

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

Minerals and phases	Symbol	Formula	Structure type	Cell edges in Å	References
Pyrite	py	(Fe,Ni) S_2	Cubic $Pa\bar{3}$	a 5.3825	Fujii <i>et al.</i> (1986)
Vaesite	vs	(Ni,Fe) S_2	Cubic $Pa\bar{3}$	a 5.6765	Nowacki <i>et al.</i> (1991)
Violarite	vl	(Fe,Ni) S_4	Cubic $Fd\bar{3}m$	a 9.465	Craig (1971)
Ni monosulfide	Nim	Ni_{1-x}S	Hexagonal $P6_3/mmc$	($x = 0$) a 3.435, c 5.350	Futami & Anzai (1984)
Monosulfide solid-solution	mss	(Fe,Ni) $_{1-x}\text{S}$	Hexagonal $P6_3/mmc$	(Fe = Ni) a 3.45, c 5.6	Craig & Scott (1976)
High-form pentlandite	hpn	(Fe,Ni) S_8	Cubic $Pn\bar{3}m$	(Fe = Ni) a 5.245 (650°C)	This study
Pentlandite	pn	(Fe,Ni) S_8	Cubic $Fm\bar{3}m$	(Fe = Ni) a 10.100	Rajamani & Prewitt (1973) Sugaki & Kitakaze (1998)
High-form godlevskite	hgd	Ni_7S_6	Hexagonal	a 3.253, c 11.359 (550°C)	This study
Godlevskite	gd	Ni_6S_6	Orthorhombic $C222$	a 9.336, b 11.219, c 9.430	Fleet (1987)
Phase β_2	β_2	Ni_4S_3 (ss)	Cubic $Pn\bar{3}m$	a 5.140 (600°C)	Kitakaze & Sugaki (2001) This study
Phase β_1	β_1	Ni_3S_2 (ss)	Cubic $Fm\bar{3}m$	a 5.210 (600°C)	Kitakaze & Sugaki (2001)
Heazlewoodite	hz	Ni_3S_2	Hexagonal $R\bar{3}2$	a 5.747, c 7.135	Fleet (1977)
Phase α ("kamacite")	α	(Fe,Ni) $\text{Fe}_{0.96}\text{Ni}_{0.06}$	Cubic $Fm\bar{3}m$	a 2.860	Ramsden & Cameron (1966)
Phase γ (taenite)	γ	(Fe,Ni) $\text{Fe}_{0.30}\text{Ni}_{0.70}$	Cubic $Fm\bar{3}m$	a 3.587	Dumpich <i>et al.</i> (1987)
Awaruite	aw	FeNi_3 (ss)	Cubic $Pm\bar{3}m$	a 3.555	Lutts & Gielen (1970)

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 μ A; curved crystals, LiF for FeK α and NiK α , and TAP for SK α . 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, β_1 and β_2 , 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 $\text{Fe}_x\text{Ni}_y\text{S}_z$ 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 β_2 ; $z = 2.00$ for vaesite, pyrite, heazlewoodite and β_1 ; $z = 1.00$ for monosulfide solid-solution; $x + y = 9.00$ for high-form pentlandite, Fe-bearing β_2 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 (FeNi_3).

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° or 1000°C, but frequently a slower heating or cooling rate of 2°, 1° or 0.3°C/min from 400° to 850°C or 850° 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 β_1 and β_2 on the Ni–S binary and their phase relations

The extensive solid-solution field of phase $\text{Ni}_{3\pm x}\text{S}_2$ 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, β_1

and β_2 with a narrow field of immiscibility between them, as determined by S activity measurement using a H_2S – H_2 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 β_1 and β_2 . To reconfirm the existence of the phases β_1 and β_2 and to obtain the relevant crystal data, high-temperature X-ray powder-diffraction was performed on synthetic Ni_3S_2 (β_1) and Ni_4S_3 (β_2) at temperatures from 500° to 700°C, because both β_1 and β_2 are unquenchable (Kitakaze & Sugaki 1996, 2001). Accordingly, β_1 and β_2 can be distinguished from each other by the difference of their powder-diffraction patterns. The phase β_1 (Ni_3S_2) is cubic $Fm\bar{3}m$ with a equal to 5.210 Å (600°C). The phase β_2 (Ni_4S_3) is cubic $Pn\bar{3}m$ 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 β_1 , β_2 , 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-diffractometry 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 β_1 and β_2 with a narrow immiscible field between them were found in place of the phase $\text{Ni}_{3\pm x}\text{S}_2$ (Fig. 1). The cell edges of the β_1 and β_2 solid-solutions decrease linearly with increasing S content (Kitakaze & Sugaki 2001). The phase β_1 at its most S-rich composition (43.0 atomic % S) breaks down to β_2 (43.3 at.% S) and liquid (42.7 at.% S) at 800°C, whereas β_2 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° \pm 3°C. On cooling, there is a eutectic point at 637° \pm 3°C and 33.2 at.% S between the β_1 (36.7 at.% S) and Ni (Lin *et al.* 1978, Singleton *et al.* 1991). The liquid disappears below this temperature. The phase β_1 with Ni_3S_2 (40.0 at.% S) inverts to heazlewoodite (low form) at 565° \pm 3°C. This transition is reversible. Also, β_1 compositions with 40.6 and 37.0 at.% S break down to mixtures of heazlewoodite (40.0 at.% S) and β_2 (~41.5 at.% S) at 564° \pm 3°C and heazlewoodite and Ni (~0.0 at.% S) at 533° \pm 3°C, respectively, at two eutectoid reactions. Phase β_2 with 43.0 at.% S breaks down to a mixture of heazlewoodite and high-form godlevskite at 524° \pm 3°C at another eutectoid.

High-form godlevskite of a composition $\text{Ni}_{6.99}\text{S}_{6.00}$ crystallizes as a result of a peritectoid reaction between β_2 and Ni monosulfide at 573° \pm 3°C, and grows to a

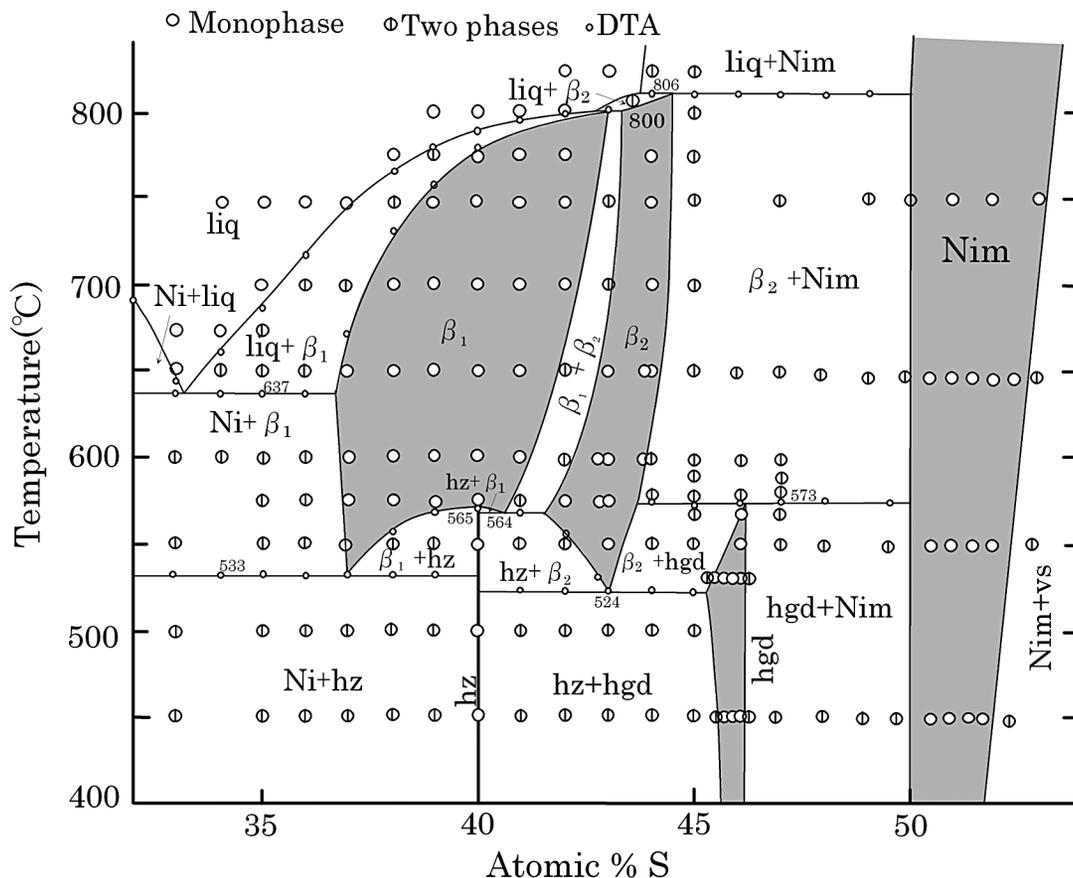


FIG. 1. The phase diagram for the composition range from 32.0 to 54.0 at.% S in the Ni–S binary at temperatures from 400° to 825°C. All phases and phase assemblages coexist with vapor. Symbols: see Table 1; liq: liquid.

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 β₂, but decreases its extent of solubility gradually with decreasing temperature. It coexists with β₂ from 573° to 524°C, with heazlewoodite from 524° to 400°C in the Ni-rich field, and Ni monosulfide from 573° to 397°C in the S-rich field (Fig. 1).

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

High-form pentlandite (Fe_{4.93}Ni_{4.07}S_{8.01}) first crystallized as a product of a peritectic reaction between monosulfide solid-solution and liquid at 870° ± 3°C, forms as a limited solid-solution from Fe_{5.06}Ni_{3.94}S_{7.92} to Fe_{3.79}Ni_{5.21}S_{7.92}, and includes the ideal composition Fe_{4.50}Ni_{4.50}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 β₂

(44.5 at.% S) on the Ni–S boundary at 806°C (Fig. 1), where phase β₂ 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 (Fe_{5.23}Ni_{3.77}S_{7.89} at 800°C) to β₂ of composition Ni_{3.74}S_{3.00} is formed at 806°C (Sugaki & Kitakaze 1996). This high-form pentlandite β₂ 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, β₁, γ, α, liquid (sulfide) and S (liquid) occur as stable phases in the system. Monosulfide solid-solution forms a complete solid-solution between Fe_{1-x}S and Ni_{1-x}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 β_2 of composition $\text{Ni}_{3.79-4.02}\text{S}_{3.00}$ at the Ni-S boundary, and coexists with γ and β_1 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 $\text{Fe}_{5.65}\text{Ni}_{3.35}\text{S}_{7.85}$. This solid solution also includes the composition of $\text{Fe}_{4.5}\text{Ni}_{4.5}\text{S}_8$ 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 β_1 appears independently as a horn-shaped solid-solution of compositions from $\text{Ni}_{2.78-3.29}\text{S}_{2.00}$ to $\text{Fe}_{0.56}\text{Ni}_{2.34}\text{S}_{2.00}$ 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 ($\text{Fe}_{0.99}\text{Ni}_{0.01}\text{S}_{1.00}$) + α ($\text{Fe}_{9.53}\text{Ni}_{0.47}$) + γ ($\text{Fe}_{8.54}\text{Ni}_{1.46}$) (Kubaschewski 1982, Swartzendruber *et al.* 1993), 2) high-form pentlandite ($\text{Fe}_{5.65}\text{Ni}_{3.35}\text{S}_{7.85}$) + monosulfide solid-solution

($\text{Fe}_{0.85}\text{Ni}_{0.13}\text{S}_{1.00}$) + γ ($\text{Fe}_{3.58}\text{Ni}_{6.42}$), 3) high-form pentlandite ($\text{Fe}_{2.61}\text{Ni}_{6.39}\text{S}_{6.99}$) + β_1 ($\text{Fe}_{0.56}\text{Ni}_{2.34}\text{S}_{2.00}$) + γ ($\text{Fe}_{2.70}\text{Ni}_{7.30}$), and 4) β_1 ($\text{Fe}_{0.33}\text{Ni}_{2.99}\text{S}_{2.00}$) + liquid ($\text{Fe}_{0.50}\text{Ni}_{6.08}\text{S}_{3.42}$) + γ ($\text{Fe}_{2.00}\text{Ni}_{8.00}$), 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 ($\text{Fe}_{0.91}\text{Ni}_{0.08}\text{S}_{2.00}$) + vaesite ($\text{Fe}_{0.19}\text{Ni}_{0.81}\text{S}_{2.00}$) + monosulfide solid-solution ($\text{Fe}_{0.66}\text{Ni}_{0.20}\text{S}_{1.00}$) or S (liquid), respectively, in the presence of vapor.

Phase relations from 650° 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 $625^\circ \pm 3^\circ\text{C}$ as a result of a polymorphic phase-transition from high-form pentlandite solid-solution of the most Fe-rich composition $\text{Fe}_{5.60}\text{Ni}_{3.40}\text{S}_{7.82}$. 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-

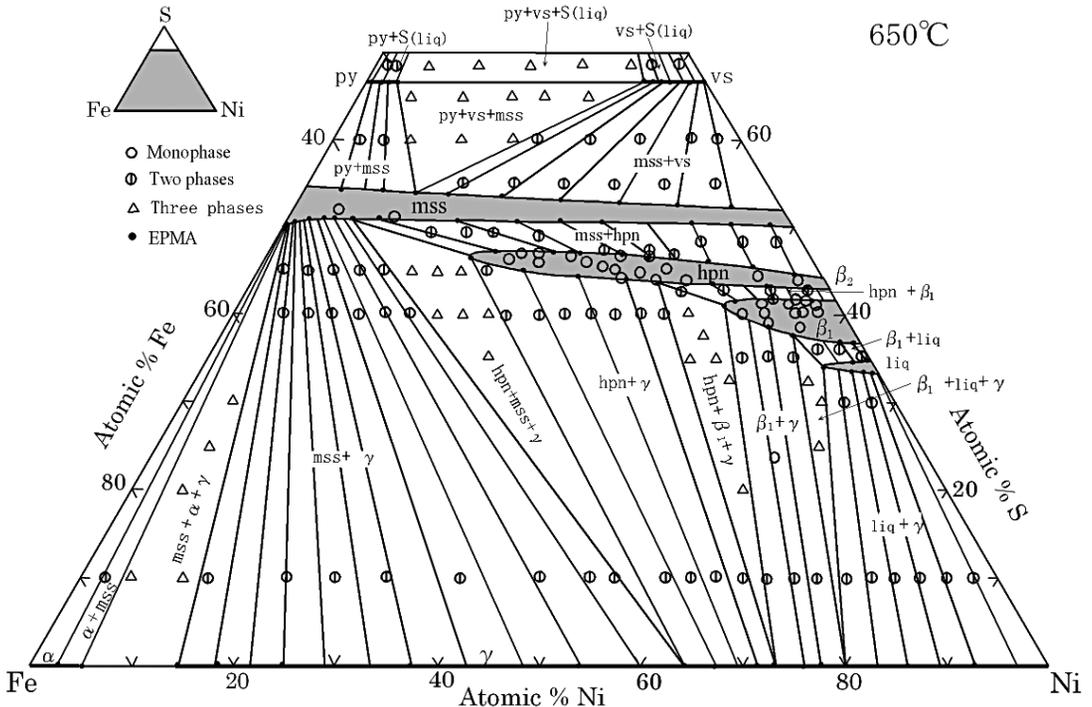


FIG. 2. The isothermal phase-diagram in the Fe-Ni-S system at 650°C. Symbols: see Table 1, liq: liquid, S(liq): sulfur liquid.

+ γ ($\text{Fe}_{8.08}\text{Ni}_{1.92}$), 2) monosulfide solid-solution ($\text{Fe}_{0.87}\text{Ni}_{0.10}\text{S}_{1.00}$) + pentlandite ($\text{Fe}_{5.64}\text{Ni}_{3.36}\text{S}_{7.82}$) + γ ($\text{Fe}_{3.78}\text{Ni}_{6.22}$), 3) pentlandite ($\text{Fe}_{3.21}\text{Ni}_{5.79}\text{S}_{7.92}$) + high-form pentlandite ($\text{Fe}_{3.19}\text{Ni}_{5.81}\text{S}_{7.89}$) + monosulfide solid-solution ($\text{Fe}_{0.40}\text{Ni}_{0.57}\text{S}_{1.00}$), 4) pentlandite ($\text{Fe}_{5.49}\text{Ni}_{3.51}\text{S}_{7.73}$) + high-form pentlandite ($\text{Fe}_{5.28}\text{Ni}_{3.72}\text{S}_{7.54}$) + γ ($\text{Fe}_{3.39}\text{Ni}_{6.61}$), and 5) high-form pentlandite ($\text{Fe}_{3.13}\text{Ni}_{5.87}\text{S}_{7.13}$) + β_1 ($\text{Fe}_{0.49}\text{Ni}_{2.52}\text{S}_{2.00}$) + γ ($\text{Fe}_{3.08}\text{Ni}_{6.92}$). The univariant assemblage 3), pentlandite + high-form pentlandite + monosulfide solid-solution, suggests that the last two phases participate in a pseudoperitectoid reaction extending the Ni-rich end of the pentlandite solid-solution. Univariant assemblage 2) indicates that the Fe-rich end of the pentlandite solid-solution extends slightly to the more Fe-rich side by means of a pseudoperitectoid reaction between monosulfide solid-solution and γ on cooling, not high-form pentlandite, because of the tie-line change from the monosulfide solid-solution + high-form pentlandite (Fe-rich end) assemblage to the Fe-rich pentlandite + γ assemblage at 617°C, as mentioned above. High-form pentlandite cannot participate in this reaction below this temperature. However, univariant assemblage 4), high-form pentlandite + pentlandite + γ , indicates that the Fe-rich extremity of high-form pentlandite retreats toward the Ni-rich side owing to its breakdown into a mixture of high-form pentlandite with a little Ni-rich composition + pentlandite + γ as a pseudoeutectoid reaction with decreasing temperature progressively below 617°C.

On the S-rich portion of the system, the compositions of pyrite and vaesite solid-solution retreat toward the Fe-S and Ni-S boundaries, respectively. In spite of this, both pyrite ($\text{Fe}_{0.94}\text{Ni}_{0.06}\text{S}_{2.00}$) and vaesite ($\text{Fe}_{0.13}\text{Ni}_{0.87}\text{S}_{2.00}$) still form two univariant assemblages separately with monosulfide solid-solution ($\text{Fe}_{0.59}\text{Ni}_{0.29}\text{S}_{1.00}$) or S (liq.) as at 600°C.

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 as its pseudoeutectoid reaction-products. New tie-lines between pentlandite and phase β_1 replace those between high-form pentlandite and phase γ at or below 579° ± 3°C. The reaction at the tie-line change was ascertained by DTA, EPMA, high-temperature X-ray diffraction and microscopic examination. This tie-line change is reversible. As a result, a new univariant assemblage, high-form pentlandite + pentlandite + β_1 appears below this temperature instead of the univariant assemblage of high-form pentlandite + pentlandite + γ . The Fe-rich extremity of high-form pentlandite furthermore retreats more to the Ni-rich

side, breaking down into a mixture of high-form pentlandite with a little Ni-rich composition + pentlandite + β_1 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 ($\alpha\text{-Ni}_7\text{S}_6$ of Kullerud & Yund 1962, Misra & Fleet 1973a) of a composition with $\text{Fe}_{0.12}\text{Ni}_{6.90}\text{S}_{6.00}$ (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 ($\text{Fe}_{0.01}\text{Ni}_{0.99}\text{S}_{1.00}$) and high-form pentlandite ($\text{Fe}_{0.03}\text{Ni}_{8.97}\text{S}_{7.04}$) 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 ($\text{Fe}_{0.23}\text{Ni}_{6.78}\text{S}_{6.00}$, 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 $\text{Fe}_{0.40}\text{Ni}_{6.61}\text{S}_{6.00}$ (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 β_1 (Ni_3S_2) at 565° ± 3°C, and then by exsolution subsequently from the solid solutions β_1 and β_2 on cooling from 565° to 533°C (eutectoid of Ni-rich β_1) and from 564° (eutectoid of S-rich β_1) to 524°C (eutectoid of β_2), respectively, at the Ni-S boundary (Fig. 1). This phase also occurs together with β_2 (Fe-free high-form pentlandite) at a S-rich eutectoid of β_1 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 β_2) and β_1 (Fe-bearing β_1) as a limited solid-solution below this temperature.

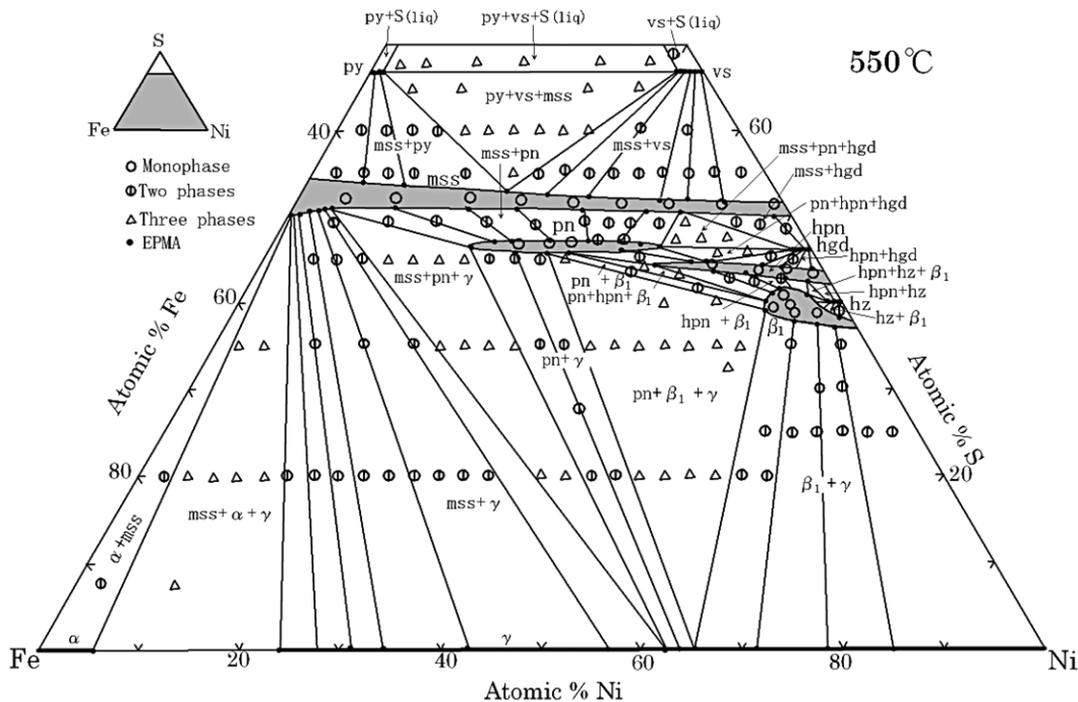


FIG. 4. The phase diagram in the system Fe–Ni–S at 550°C. Symbols: see Table 1, S(liq): sulfur liquid.

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, β_1 and γ . However, an assemblage of pentlandite and heazlewoodite cannot form because of the stable tie-lines between high-form pentlandite and β_1 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 $Ni_{3.91-4.13}S_{3.00}$ (β_2) at 550°C. It coexists with high-form godlevskite, β_1 or heazlewoodite (or both) besides pentlandite. A β_1 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_3S_2 to $Fe_{0.06}Ni_{2.95}S_{2.00}$ 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 ($Fe_{2.62}Ni_{6.38}S_{7.16}$) + β_1 ($Fe_{0.36}Ni_{2.63}S_{2.00}$), 4) high-form pentlandite ($Fe_{0.28}Ni_{8.72}S_{6.68}$) + heazlewoodite ($Fe_{0.06}Ni_{2.95}S_{2.00}$) + β_1 ($Fe_{0.14}Ni_{2.74}S_{2.00}$), and 5) pentlandite ($Fe_{4.39}Ni_{4.61}S_{7.70}$) + β_1 ($Fe_{0.41}Ni_{2.70}S_{2.00}$) + γ ($Fe_{3.47}Ni_{6.53}$) 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 ($Fe_{0.52}Ni_{0.39}S_{1.00}$) 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 β_1 disappears at $533^\circ \pm 3^\circ\text{C}$ 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 β_1 coexists with pentlandite, high-form pentlandite (Fe-bearing β_2), heazlewoodite and γ (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 β_2 breaks down to a mixture of heazlewoodite and high-form godlevskite at $524^\circ \pm 3^\circ\text{C}$ and 43.0 at.% S as a result of a eutectoid on the Ni-S boundary, but its solid solution (high-form pentlandite) still remains as a Ni-rich ternary phase within a small thin field of compositions from $\text{Fe}_{1.32}\text{Ni}_{7.68}\text{S}_{6.85}$ to $\text{Fe}_{0.47}\text{Ni}_{8.53}\text{S}_{6.82}$ near the Ni-S boundary at 520°C (Fig. 5), coexisting with heazlewoodite, β_1 , high-form godlevskite or pentlandite (or both). Pentlandite coexists separately with monosulfide solid-solution, high-form godlevskite, β_1 , or γ (or both) in addition to high-form pentlandite solid-solution, but it cannot coexist with heazlewoodite because the tie-lines between high-form pentlandite solid-solution and β_1 are stable at 520°C.

Seven univariant assemblages in the Ni-rich side of the system at 520°C are found in Figure 5, as follows: 1) pentlandite ($\text{Fe}_{2.40}\text{Ni}_{6.60}\text{S}_{7.89}$) + monosulfide solid-solution ($\text{Fe}_{0.15}\text{Ni}_{0.82}\text{S}_{1.00}$) + high-form godlevskite ($\text{Fe}_{0.40}\text{Ni}_{6.61}\text{S}_{6.00}$), 2) pentlandite ($\text{Fe}_{2.44}\text{Ni}_{6.56}\text{S}_{7.85}$) + high-form pentlandite ($\text{Fe}_{1.10}\text{Ni}_{7.90}\text{S}_{6.96}$) + high-form godlevskite ($\text{Fe}_{0.42}\text{Ni}_{6.65}\text{S}_{6.00}$), 3) pentlandite ($\text{Fe}_{3.52}\text{Ni}_{5.48}\text{S}_{7.82}$) + high-form pentlandite ($\text{Fe}_{1.32}\text{Ni}_{7.68}\text{S}_{6.85}$) + β_1 ($\text{Fe}_{0.36}\text{Ni}_{2.70}\text{S}_{2.00}$), 4) pentlandite ($\text{Fe}_{4.25}\text{Ni}_{4.75}\text{S}_{7.73}$) + β_1 ($\text{Fe}_{0.36}\text{Ni}_{2.75}\text{S}_{2.00}$) + γ ($\text{Fe}_{3.48}\text{Ni}_{6.52}$), 5) high-form godlevskite ($\text{Fe}_{0.09}\text{Ni}_{6.98}\text{S}_{6.00}$) + high-form pentlandite ($\text{Fe}_{0.47}\text{Ni}_{8.53}\text{S}_{6.82}$) + heazlewoodite ($\text{Fe}_{0.04}\text{Ni}_{2.95}\text{S}_{2.00}$), 6) high-form pentlandite ($\text{Fe}_{0.54}\text{Ni}_{8.46}\text{S}_{6.82}$) + β_1 ($\text{Fe}_{0.20}\text{Ni}_{2.61}\text{S}_{2.00}$) + heazlewoodite ($\text{Fe}_{0.11}\text{Ni}_{2.90}\text{S}_{2.00}$), and 7) β_1 ($\text{Fe}_{0.12}\text{Ni}_{3.22}\text{S}_{2.00}$) + heazlewoodite ($\text{Fe}_{0.01}\text{Ni}_{3.00}\text{S}_{2.00}$) + γ ($\text{Fe}_{2.98}\text{Ni}_{7.02}$).

Awaruite ($\text{Fe}_{2.80}\text{Ni}_{7.20}$) appears as a result of an order-disorder transformation of γ 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 γ (or both) below 517°C.

The tie-lines between high-form pentlandite and heazlewoodite are replaced by those between high-form godlevskite and β_1 at $512^\circ \pm 3^\circ\text{C}$ or below. This tie-

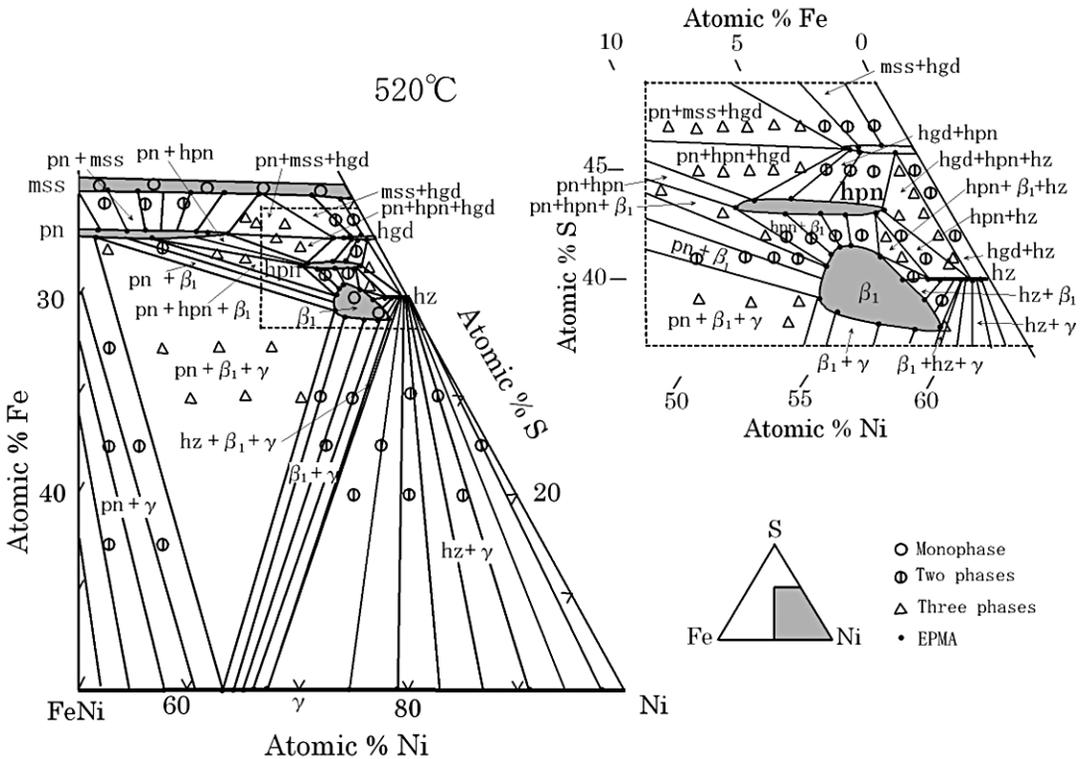


FIG. 5. The partial phase-diagram in the Fe-Ni-S system at 520°C. Symbols: see Table 1.

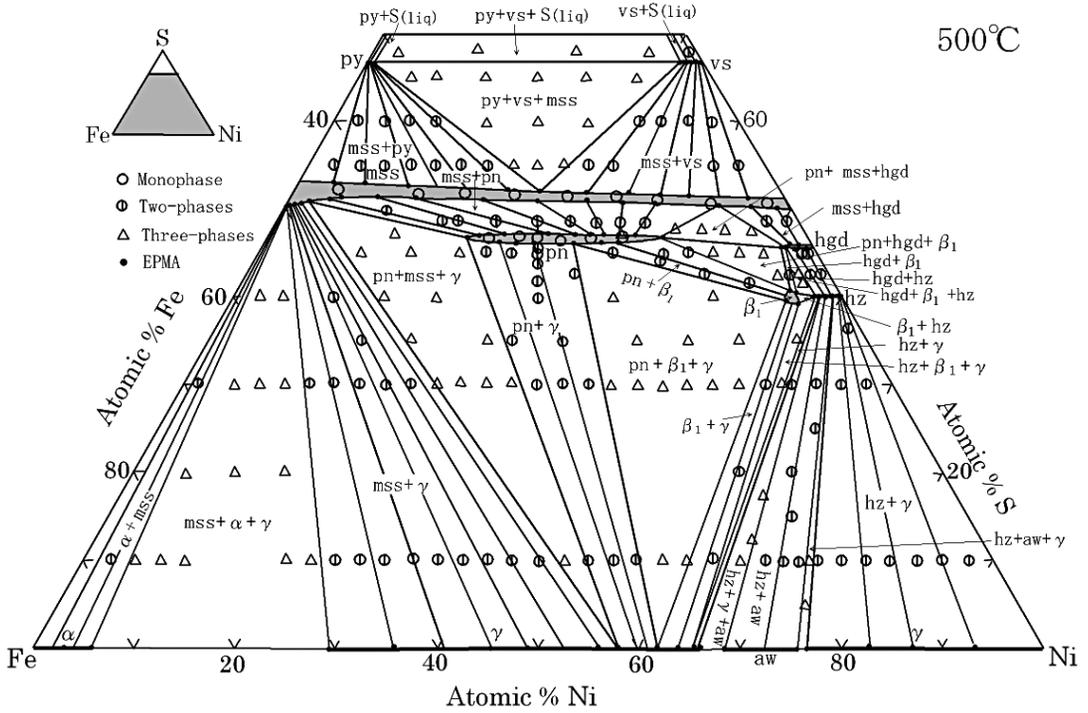


FIG. 6. The phase diagram in the Fe–Ni–S system at 500°C. See Table 1 for symbols, S(liq): sulfur liquid.

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, β_1 and high-form godlevskite at $503^\circ \pm 3^\circ\text{C}$ 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, $\text{Fe}_{0.20}\text{Ni}_{2.67}\text{S}_{2.00}$ for β_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, β_1 or γ (or both), as shown in Figure 6. Pentlandite cannot coexist with heazlewoodite because of the stable tie-lines between high-form godlevskite and β_1 at 500°C . The monosulfide solid-solution field

becomes narrower but still extends continuously across the entire diagram. High-form godlevskite coexists with β_1 or heazlewoodite (or both) in addition to monosulfide solid-solution or pentlandite (or both), but cannot coexist with γ or awaruite owing to the tie-lines of β_1 and pentlandite or heazlewoodite. Heazlewoodite coexists stably with γ or awaruite (or both) as well as β_1 or high-form godlevskite (or both). Awaruite coexists only with heazlewoodite or γ (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 ($\text{Fe}_{0.99}\text{Ni}_{0.01}\text{S}_{1.00}$) + α ($\text{Fe}_{9.43}\text{Ni}_{0.57}$) + γ ($\text{Fe}_{7.04}\text{Ni}_{2.96}$) (Kubaschewski 1982, Swartzendruber *et al.* 1993), 2) pentlandite ($\text{Fe}_{5.68}\text{Ni}_{3.32}\text{S}_{7.85}$) + monosulfide solid-solution ($\text{Fe}_{0.92}\text{Ni}_{0.04}\text{S}_{1.00}$) + γ ($\text{Fe}_{4.20}\text{Ni}_{5.80}$), 3) pentlandite ($\text{Fe}_{2.43}\text{Ni}_{6.57}\text{S}_{7.85}$) + monosulfide solid-solution ($\text{Fe}_{0.13}\text{Ni}_{0.84}\text{S}_{1.00}$) + high-form godlevskite ($\text{Fe}_{0.40}\text{Ni}_{6.58}\text{S}_{6.00}$), 4) pentlandite ($\text{Fe}_{2.44}\text{Ni}_{6.56}\text{S}_{7.85}$) + high-form godlevskite ($\text{Fe}_{0.40}\text{Ni}_{6.61}\text{S}_{6.00}$) + β_1 ($\text{Fe}_{0.20}\text{Ni}_{2.67}\text{S}_{2.00}$), 5) high-form godlevskite ($\text{Fe}_{0.34}\text{Ni}_{6.70}\text{S}_{6.00}$) + β_1 ($\text{Fe}_{0.20}\text{Ni}_{2.70}\text{S}_{2.00}$) + heazlewoodite ($\text{Fe}_{0.13}\text{Ni}_{2.87}\text{S}_{2.00}$), 6) pentlandite ($\text{Fe}_{3.79}\text{Ni}_{5.21}\text{S}_{7.76}$) + β_1 ($\text{Fe}_{0.31}\text{Ni}_{2.81}\text{S}_{2.00}$) + γ ($\text{Fe}_{3.80}\text{Ni}_{6.20}$), 7) heazlewoodite ($\text{Fe}_{0.13}\text{Ni}_{2.87}\text{S}_{2.00}$) + β_1 ($\text{Fe}_{0.25}\text{Ni}_{2.91}\text{S}_{2.00}$) + γ ($\text{Fe}_{3.48}\text{Ni}_{6.52}$), 8) heazlewoodite ($\text{Fe}_{0.10}\text{Ni}_{2.93}\text{S}_{2.00}$) + γ ($\text{Fe}_{3.43}\text{Ni}_{6.57}$) + awaruite

($\text{Fe}_{3.15}\text{Ni}_{6.85}$) (Kubaschewski 1982, Swartzendruber *et al.* 1993), and 9) heazlewoodite ($\text{Fe}_{0.06}\text{Ni}_{2.95}\text{S}_{2.00}$) + awaruite ($\text{Fe}_{2.44}\text{Ni}_{7.56}$) + γ ($\text{Fe}_{2.35}\text{Ni}_{7.65}$) (Kubaschewski 1982, Swartzendruber *et al.* 1993).

Meanwhile, in the S-rich portion of the system, pyrite ($\text{Fe}_{0.99}\text{Ni}_{0.02}\text{S}_{2.00}$) and vaesite ($\text{Fe}_{0.06}\text{Ni}_{0.94}\text{S}_{2.00}$) at 500°C still form two univariant assemblages with 10) monosulfide solid-solution ($\text{Fe}_{0.45}\text{Ni}_{1.047}\text{S}_{1.00}$) 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 β_1 and high-form godlevskite are replaced by those between pentlandite and heazlewoodite at $498^\circ \pm 3^\circ\text{C}$. 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 β_1 field contracts with decreasing temperature, and finally disappears by its breakdown to a mixture of pentlandite, heazlewoodite and γ at $484^\circ \pm 3^\circ\text{C}$ at a ternary eutectoid. The composition of the β_1 at this eutectoid is very close to that of the β_1 ($\text{Fe}_{0.26}\text{Ni}_{2.87}\text{S}_{2.00}$) produced at $485^\circ \pm 3^\circ\text{C}$. Also, the compositions of the breakdown products at the eutectoid are close to those of pentlandite

($\text{Fe}_{3.23}\text{Ni}_{5.77}\text{S}_{7.76}$), heazlewoodite ($\text{Fe}_{0.11}\text{Ni}_{2.90}\text{S}_{2.00}$), and γ ($\text{Fe}_{3.49}\text{Ni}_{6.51}$) 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 β_1 and the lack of crystallization of violarite. We found nine univariant assemblages, as follows: 1) monosulfide solid-solution ($\text{Fe}_{0.99}\text{Ni}_{0.01}\text{S}_{1.00}$) + α ($\text{Fe}_{9.45}\text{Ni}_{0.55}$) + γ ($\text{Fe}_{6.45}\text{Ni}_{3.55}$), 2) monosulfide solid-solution ($\text{Fe}_{0.92}\text{Ni}_{0.04}\text{S}_{1.00}$) + pentlandite ($\text{Fe}_{5.70}\text{Ni}_{3.30}\text{S}_{7.85}$) + γ ($\text{Fe}_{4.56}\text{Ni}_{5.44}$), 3) pentlandite ($\text{Fe}_{2.62}\text{Ni}_{6.38}\text{S}_{7.82}$) + monosulfide solid-solution ($\text{Fe}_{0.13}\text{Ni}_{0.85}\text{S}_{1.00}$) + high-form godlevskite ($\text{Fe}_{0.16}\text{Ni}_{6.86}\text{S}_{6.00}$), 4) pentlandite ($\text{Fe}_{2.62}\text{Ni}_{6.38}\text{S}_{7.82}$) + high-form godlevskite ($\text{Fe}_{0.16}\text{Ni}_{6.86}\text{S}_{6.00}$) + heazlewoodite ($\text{Fe}_{0.08}\text{Ni}_{2.92}\text{S}_{2.00}$), 5) pentlandite ($\text{Fe}_{3.44}\text{Ni}_{5.56}\text{S}_{7.76}$) + heazlewoodite ($\text{Fe}_{0.08}\text{Ni}_{2.92}\text{S}_{2.00}$) + γ ($\text{Fe}_{4.16}\text{Ni}_{5.84}$), 6) heazlewoodite ($\text{Fe}_{0.06}\text{Ni}_{2.93}\text{S}_{2.00}$) + γ ($\text{Fe}_{3.91}\text{Ni}_{6.09}$) + awaruite ($\text{Fe}_{3.32}\text{Ni}_{6.68}$), 7) heazlewoodite ($\text{Fe}_{0.03}\text{Ni}_{2.97}\text{S}_{2.00}$) + awaruite ($\text{Fe}_{2.20}\text{Ni}_{7.80}$) + γ ($\text{Fe}_{2.05}\text{Ni}_{7.95}$), 8) and 9) pyrite ($\text{Fe}_{0.99}\text{Ni}_{0.01}\text{S}_{2.00}$) + vaesite ($\text{Fe}_{0.01}\text{Ni}_{0.99}\text{S}_{2.00}$) + monosulfide solid-solution ($\text{Fe}_{0.39}\text{Ni}_{0.50}\text{S}_{1.00}$) or S (liquid).

Violarite of composition $\text{Fe}_{0.70}\text{Ni}_{2.29}\text{S}_{4.00}$ (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

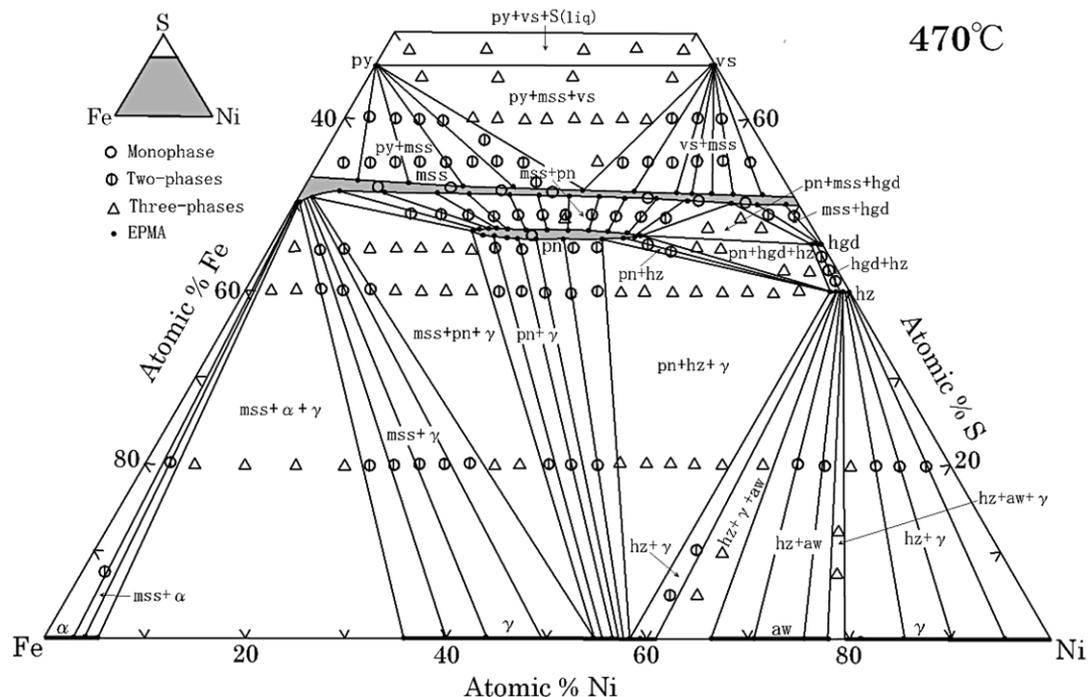


FIG. 7. The phase diagram in the Fe-Ni-S system at 470°C. See Table 1 for symbols: S(liq) : sulfur liquid.

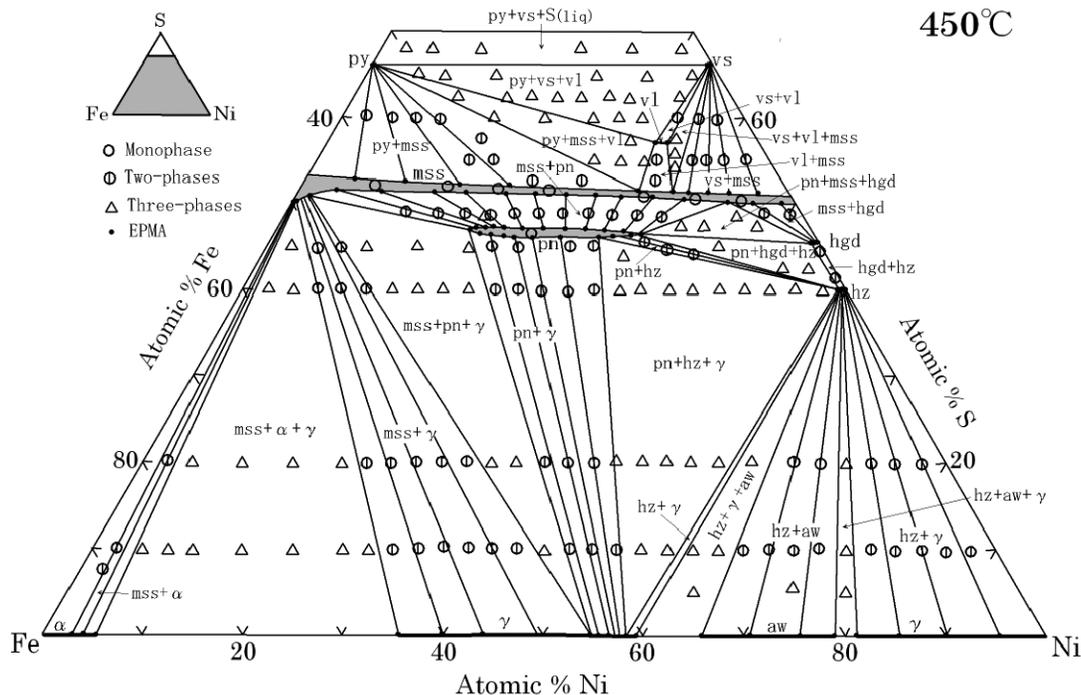


FIG. 8. The phase relations in the system Fe–Ni–S at 450°C. See Table 1 for symbols, S(liq): sulfur liquid.

monosulfide solid-solution ($\text{Fe}_{0.32}\text{Ni}_{0.63}\text{S}_{1.00}$ at 460°C) and vaesite ($\text{Fe}_{0.01}\text{Ni}_{0.99}\text{S}_{2.00}$ at 460°C) at $459^\circ \pm 3^\circ\text{C}$, 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_1 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 thin. 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 $\text{Fe}_{5.73}\text{Ni}_{3.27}\text{S}_{7.92}$ to $\text{Fe}_{2.84}\text{Ni}_{6.16}\text{S}_{7.89}$, including $\text{Fe}_{4.5}\text{Ni}_{4.5}\text{S}_{8.0}$, but becomes thinner than that at 500°C. We recognize seven univariant assemblages as follows: 1) monosulfide solid-solution ($\text{Fe}_{0.99}\text{Ni}_{0.01}\text{S}_{1.00}$) + α ($\text{Fe}_{9.41}\text{Ni}_{0.59}$) + γ ($\text{Fe}_{6.42}\text{Ni}_{3.58}$), 2) monosulfide solid-solution ($\text{Fe}_{0.95}\text{Ni}_{0.03}\text{S}_{1.00}$) + pentlandite ($\text{Fe}_{5.73}\text{Ni}_{3.27}\text{S}_{7.92}$) + γ ($\text{Fe}_{4.55}\text{Ni}_{5.45}$), 3) pentlandite ($\text{Fe}_{2.84}\text{Ni}_{6.16}\text{S}_{7.89}$) + monosulfide solid-solution ($\text{Fe}_{0.13}\text{Ni}_{0.86}\text{S}_{1.00}$) + high-form godlevskite ($\text{Fe}_{0.05}\text{Ni}_{6.94}\text{S}_{6.00}$), 4) pentlandite ($\text{Fe}_{2.84}\text{Ni}_{6.16}\text{S}_{7.89}$) + high-form godlevskite ($\text{Fe}_{0.05}\text{Ni}_{6.94}\text{S}_{6.00}$) + heazlewoodite ($\text{Fe}_{0.04}\text{Ni}_{2.95}\text{S}_{2.00}$), 5) pentlandite ($\text{Fe}_{3.61}\text{Ni}_{5.39}\text{S}_{7.73}$) + heazlewoodite ($\text{Fe}_{0.04}\text{Ni}_{2.97}\text{S}_{2.00}$) + γ ($\text{Fe}_{4.17}\text{Ni}_{5.83}$), 6) heazlewoodite ($\text{Fe}_{0.02}\text{Ni}_{2.97}\text{S}_{2.00}$) + γ ($\text{Fe}_{4.08}\text{Ni}_{5.92}$) + awaruite ($\text{Fe}_{3.43}\text{Ni}_{6.57}$), and 7) heazlewoodite ($\text{Fe}_{0.02}\text{Ni}_{3.00}\text{S}_{2.00}$) + awaruite ($\text{Fe}_{2.11}\text{Ni}_{7.89}$) + γ ($\text{Fe}_{1.88}\text{Ni}_{8.12}$) 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 $\text{Fe}_{0.64}\text{Ni}_{2.37}\text{S}_{4.00}$ to $\text{Fe}_{0.71}\text{Ni}_{2.29}\text{S}_{4.00}$ at 450°C. There are four more univariant assemblages in the S-rich portion of the system: 8) pyrite ($\text{Fe}_{0.99}\text{Ni}_{0.01}\text{S}_{2.00}$) + violarite ($\text{Fe}_{0.71}\text{Ni}_{2.29}\text{S}_{4.00}$) + vaesite ($\text{Fe}_{0.02}\text{Ni}_{0.99}\text{S}_{2.00}$), 9) pyrite ($\text{Fe}_{0.99}\text{Ni}_{0.01}\text{S}_{2.00}$) +

violarite ($\text{Fe}_{0.71}\text{Ni}_{2.29}\text{S}_{4.00}$) + monosulfide solid-solution ($\text{Fe}_{0.27}\text{Ni}_{0.65}\text{S}_{1.00}$), and 10) vaesite ($\text{Fe}_{0.01}\text{Ni}_{0.99}\text{S}_{2.00}$) + violarite ($\text{Fe}_{0.64}\text{Ni}_{2.37}\text{S}_{4.00}$) + monosulfide solid-solution ($\text{Fe}_{0.23}\text{Ni}_{0.72}\text{S}_{1.00}$) 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 $431^\circ \pm 3^\circ\text{C}$, however.

PHASE RELATIONS OF THE $\text{Fe}_{4.5}\text{Ni}_{4.5}\text{-S}$
AND $\text{Fe}_{0.9}\text{S-Ni}_3\text{S}_2$ JOINS IN THE SYSTEM Fe-Ni-S

Phase relations along the $\text{Fe}_{4.5}\text{Ni}_{4.5}\text{-S}$ join

The phase relations were investigated along the pseudobinary $\text{Fe}_{4.5}\text{Ni}_{4.5}\text{-S}$ 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 $\text{Fe}_{4.5}\text{Ni}_{4.5}\text{S}_{8.0}$, is cubic $Fm\bar{3}m$ with an a parameter of 10.100 \AA at room temperature. On the other hand, high-form pentlandite ($\text{Fe}_{4.5}\text{Ni}_{4.5}\text{S}_{7.95}$) is cubic $Pn\bar{3}m$ with an a of 5.194 \AA 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 $\text{Fe}_{4.5}\text{Ni}_{4.5}\text{S}_{7.36}$ (44.98 atomic % S) at $587^\circ \pm 3^\circ\text{C}$, corresponding to the end of the exsolution and the beginning of the pseudoeutectoid

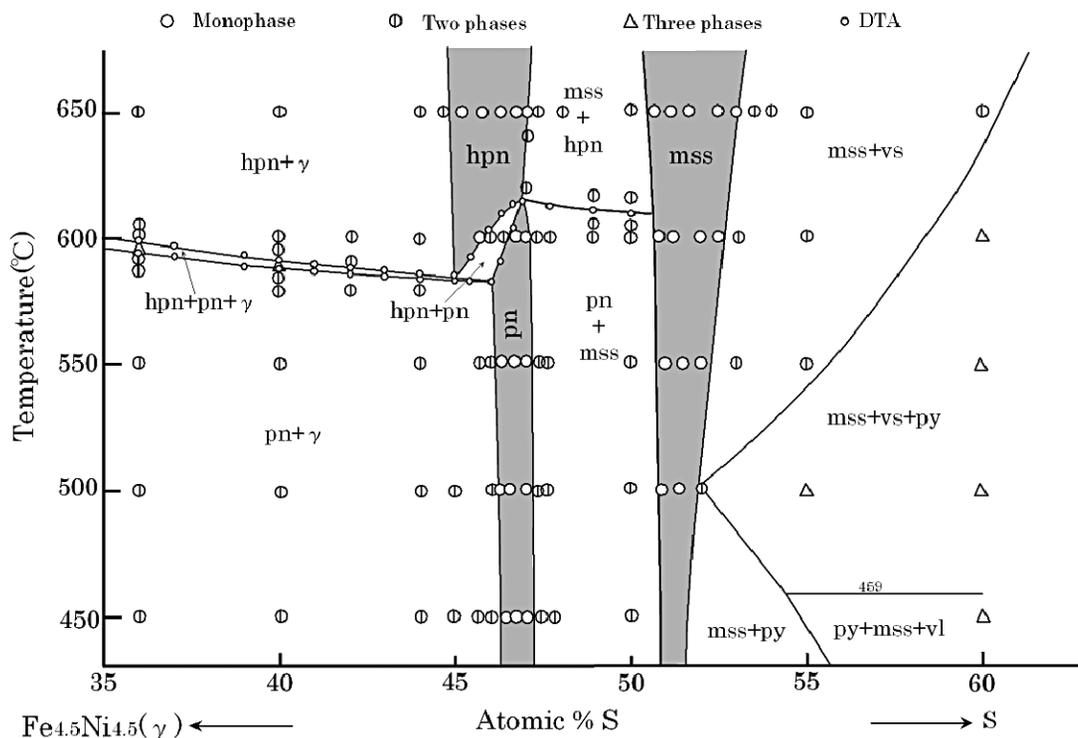


FIG. 9. The phase relations of the $\text{Fe}_{4.5}\text{Ni}_{4.5}\text{-S}$ join in the composition range from 35 to 60 at.% S at temperatures from 650° to 450°C in the Fe-Ni-S system. See Table 1 for symbols.

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 γ at 587°C, and changes successively to the divariant assemblage pentlandite and γ 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–Ni₃S₂ join

We considered a pseudobinary phase-diagram for the join Fe_{0.9}S–Ni₃S₂ (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, β_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 β_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 β_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, β_1 , high-form godlevskite, and heazlewoodite or γ (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

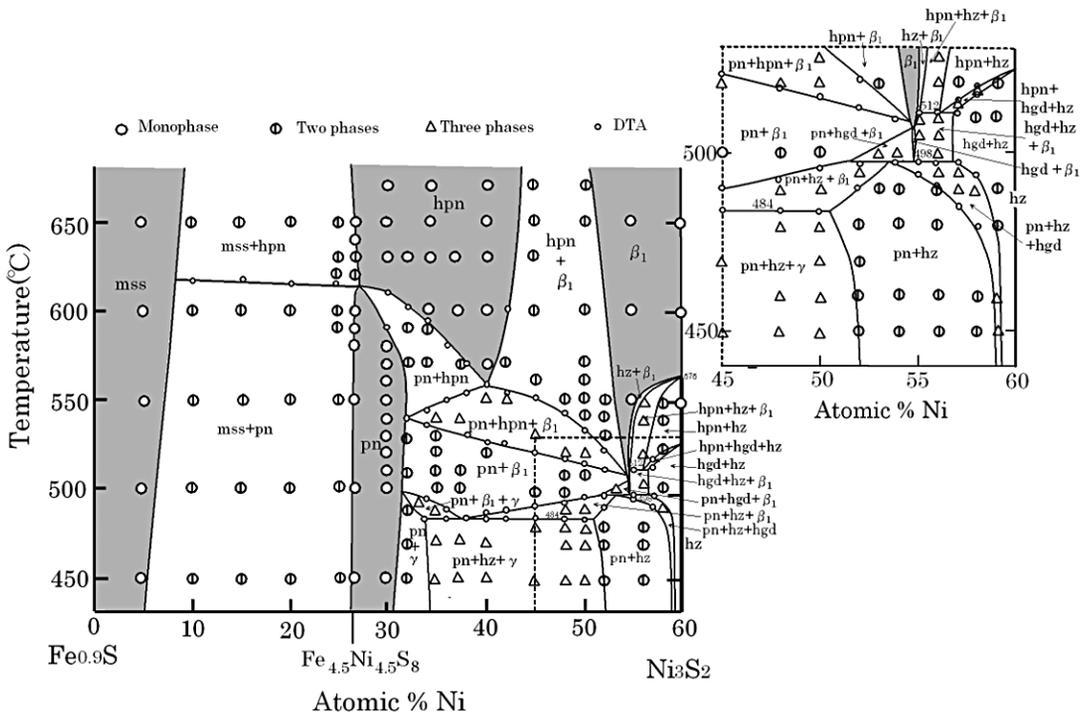


FIG. 10. The phase relations in the Fe_{0.9}S–Ni_{3.0}S_{2.0} join of the system Fe–Ni–S at the temperatures from 650° to 450°C in the composition from 0 to 60 at. % Ni. See Table 1 for symbols. At 512°C, the tie-line changes between high-form pentlandite + heazlewoodite (high temperature) and high-form godlevskite + β_1 (low temperature) (see inset).

phase transition begins from high-form pentlandite with $\text{Fe}_{4.42}\text{Ni}_{4.58}\text{S}_{7.96}$ (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 β_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 β_1 below this temperature. High-form pentlandite (Fe-bearing β_2) is stable down to 503°C of its eutectoid in the system, but the fields of the univariant assemblage high-form pentlandite + pentlandite + β_1 disappear at a higher temperature (540° to 509°C) than 503°C because those are off the join. The divariant assemblage high-form pentlandite + β_1 also disappears at 509°C.

Phase β_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 β_1 field actually lies off the join. But β_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 γ (or both) at temperatures from 565° to 484°C, as seen in the phase diagram (Fig. 10).

Heazlewoodite with Ni_3S_2 on the join first appears as a stable principal phase owing to the phase transition of β_1 at 565°C, and coexists with β_1 (565° to 484°C), high-form pentlandite (565° to 512°C), high-form godlevskite (524° to 397°C), pentlandite (below 498°C) and γ (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 β_1 , high-form godlevskite or γ . The univariant assemblage pentlandite, heazlewoodite and β_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 γ 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 β_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 β_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 ($\text{Fe}_{5.60}\text{Ni}_{3.40}\text{S}_{7.82}$ at 625°C) at temperatures from 617° to 503°C ($\text{Fe}_{1.04}\text{Ni}_{7.96}\text{S}_{6.93}$). 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 + γ at temperatures from 617° to 579°C and high-form pentlandite + pentlandite + β_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 β_2) + high-form godlevskite + heazlewoodite at temperatures from 524° to 512°C as the curve **gh** and high-form pentlandite + high-form godlevskite + β_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 $\text{Fe}_{1.04}\text{Ni}_{7.96}\text{S}_{6.93}$ (6.5Fe, 50.0Ni, 43.5S in at.%). Thus, high-form pentlandite (Fe-bearing β_2) finally breaks down to a mixture of pentlandite ($\text{Fe}_{2.44}\text{Ni}_{6.56}\text{S}_{7.85}$), high-form godlevskite ($\text{Fe}_{0.40}\text{Ni}_{6.61}\text{S}_{6.00}$) and β_1 ($\text{Fe}_{0.20}\text{Ni}_{2.67}\text{S}_{2.00}$), 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 β_1 (above 650° to 503°C) and heazlewoodite (564° to 512°C) (Fig. 11).

The β_1 solid-solution

Phase β_1 also reduces its field with decreasing temperature. In this case, we document four paths of the pseudoeutectoid reactions of the β_1 solid-solution

Exsolution of the β_1 solid-solution from high-form pentlandite, pentlandite, high-form godlevskite, heazlewoodite and γ , in addition to the pseudoeutectoid reactions of β_1 mentioned above, also reduce its field with decreasing temperature. Concretely, exsolution of the β_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° (~700°) to 503°C 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° to 484°C for the metal-rich boundary of pentlandite, a small field surrounded by the curves **mn**, **no** and **mo** (Ni-rich side) from 512° to 498°C for high-form godlevskite, an area enclosed by the curves **lm**, **mo** (Ni-rich side), **oq** and **pq** from 564° to 484°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° (~700°C) to 484°C for γ .

Finally, β_1 breaks down to a mixture of pentlandite ($\text{Fe}_{3.23}\text{Ni}_{5.77}\text{S}_{7.79}$) + heazlewoodite ($\text{Fe}_{0.11}\text{Ni}_{2.90}\text{S}_{2.00}$) + γ ($\text{Fe}_{3.49}\text{Ni}_{6.51}$) at a ternary eutectoid, 484° ± 3°C and $\text{Fe}_{0.26}\text{Ni}_{2.87}\text{S}_{2.00}$, and disappears below this temperature. The phase β_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 γ , respectively.

DISCUSSION AND SUMMARY

High-low inversion of pentlandite

Kullerud (1962, 1963a) carried out experiments to document the thermal stability of pentlandite ($\text{Fe}_{4.5}\text{Ni}_{4.5}\text{S}_8$) 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°C on heating, interpreted to be a breakdown of pentlandite and not its polymorphic inversion because the peak of the DTA at 610°C required a larger latent heat anomaly than that of a second peak, involving melting at 863°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 $\text{Ni}_{3\pm}\text{S}_2$ (high-form heazlewoodite). Therefore, it is a possibility that high-

form pentlandite was misidentified with phase $\text{Ni}_{3\pm}\text{S}_2$ 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° and 800°C, respectively, transforms to pentlandite (low form) at 600° and 25°C reversibly in a representative 110 precession photograph for a single crystal with a composition, for example, $\text{Fe}_{4.56}\text{Ni}_{4.84}\text{S}_{7.95}$. 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°C (Fig. 2) in this study. However, the area of its field is smaller than that of the $(\text{Ni,Fe})_{3\pm}\text{S}_2$ solid-solution at 725°C found by Karup-Møller & Makovicky (1995) because our high-form field does not include a β_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°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 β_1 at a ternary eutectoid, 503°C and $\text{Fe}_{1.04}\text{Ni}_{7.96}\text{S}_{6.93}$, and disappears completely below this temperature in the system.

High-form pentlandite solid-solution

No phase corresponding to high-form pentlandite solid-solution, including $\text{Fe}_{4.5}\text{Ni}_{4.5}\text{S}_{8.0}$, was found at temperatures above 610°C by Kullerud (1963a, 1963b), Kullerud *et al.* (1969) and Craig & Kullerud (1969), although they reported the appearance of Ni-rich ternary phase $(\text{Ni,Fe})_{3\pm}\text{S}_2$ at 862°C whose solid-solution field approached the Ni-S boundary with decreasing temperature. Hsieh *et al.* (1982) also showed the existence of a β solid-solution as a small lenticular field of a ternary composition near a liquid field at 850°C. Their β phase has more Ni-rich and S-poor compositions than $\text{Fe}_{4.5}\text{Ni}_{4.5}\text{S}_8$, but is located within a field of liquid or near its S-rich boundary in the isotherm at 850°C by Sugaki & Kitakaze (1998). Sugaki *et al.* (1983, 1984) found an extensive field of high-form pentlandite from more Fe-rich compositions than $\text{Fe}_{4.5}\text{Ni}_{4.5}\text{S}_{8.0}$ to $\text{Ni}_{3\pm}\text{S}_2$ of the Ni-S boundary at 800° and 650°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°, 650° and 600°C. 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 ($\text{Fe}_x\text{Ni}_{1-x}$) $_{3\pm y}\text{S}_2$ at 820° and 600°C. Karup-Møller & Makovicky (1995) also showed an elongate field of $(\text{Ni,Fe})_{3\pm x}\text{S}_2$ 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 $\text{Ni}_{3\pm x}\text{S}_2$ solid-solution of Sugaki *et al.* (1984).

Note that $\text{Ni}_{3\pm x}\text{S}_2$ is not a single phase, but consists of β_1 and β_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 β_1 or β_2 could coexist with the high-form pentlandite solid-solution. As a result, it was proved that the high-form pentlandite solid-solution and β_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 β_2 , in comparison with β_1 , are more similar to those of high-form pentlandite, where Fe = Ni. This high-form pentlandite β_2 solid-solution is maintained at temperatures from 806° to 503°C. Phase β_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 $\text{Ni}_{3\pm x}\text{S}_2$ solid-solution at 650°C of Sugaki *et al.* (1984) and Hayashi (1985), heazlewoodite solid-solution at 600°C of Fedorova & Sinyakova (1993) and $(\text{Ni,Fe})_{3\pm x}\text{S}_2$ at 725°C of Karup-Møller & Makovicky (1995), include the β_1 composition and lie outside of the composition of β_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 β_1 within the solid-solution field. However, their interpretation of phase relations at 820°C, for which no β_1 and β_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 $\text{Fe}_x\text{Ni}_{9-x}\text{S}_8$ ($x = 5.5$ 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 $\text{Fe}_{3.5}\text{Ni}_{5.5}\text{S}$ join are approximately 47.1 at.% S, except for around the Fe-rich end ($\text{Fe}_{5.65}\text{Ni}_{3.35}\text{S}_{7.82}$; 33.6 Fe, 19.9 Ni, 46.5 S in at.%) 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 $\text{Fe}_x\text{Ni}_{9-x}\text{S}$ join became poorer in S than 47.06 at.% S, such as $\text{Fe}_{3.50}\text{Ni}_{5.50}\text{S}_{7.98}$ (47.00 at.% S), $\text{Fe}_{3.0}\text{Ni}_{6.0}\text{S}_{7.95}$ (46.90 at.% S), $\text{Fe}_{2.9}\text{Ni}_{6.1}\text{S}_{7.92}$ (46.81 at.% S) and $\text{Fe}_{2.5}\text{Ni}_{6.5}\text{S}_{7.85}$ (46.59 at.% S) with increasing Ni content.

High-form pentlandite (Fe-bearing β_2) of a composition very close to $\text{Fe}_{1.04}\text{Ni}_{7.96}\text{S}_{6.93}$ at 505°C finally breaks down to a mixture of pentlandite, β_1 and high-form godlevskite in a eutectoid reaction at $503^\circ \pm 3^\circ\text{C}$. This temperature is approximately similar to that of the heazlewoodite solid-solution found by Fedorova & Sinyakova (1993), although the reaction is more complicated in their phase diagram because the solid-solution encloses β_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 γ 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 + γ (above 650° to 617°C), 2) high-form pentlandite + pentlandite + γ (617° to 579°C), 3) pentlandite + high-form pentlandite + β_1 (579° to 503°C), 4) high-form pentlandite + β_1 + γ (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 + β_1 + heazlewoodite (564° to 512°C), and 9) high-form pentlandite + high-form godlevskite + β_1 (512° to 503°C) (Fig. 11). Among them, the four univariant assemblages (3, 4, 8 and 9) coexisting with β_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-rich side with decreasing temperature. A compositional range from $\text{Fe}_{5.68}\text{Ni}_{3.32}\text{S}_{7.85}$ to $\text{Fe}_{2.43}\text{Ni}_{6.57}\text{S}_{7.85}$ (46.59 at.% S) including $\text{Fe}_{4.5}\text{Ni}_{4.5}\text{S}_8$ 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 $\text{FeS}-(\text{Ni,Fe})_{3\pm 1}\text{S}_2$ 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 $498^\circ \pm 3^\circ\text{C}$ 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 $\text{Fe}_{3.0}\text{Ni}_{6.0}\text{S}_{8.0}$ and $\text{Fe}_{2.5}\text{Ni}_{6.5}\text{S}_{8.0}$ undergoes a phase transition of non-mass-transfer type at 603° and $597^\circ \pm 3^\circ\text{C}$, 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 ($\text{Fe}_{3.0}\text{Ni}_{6.0}\text{S}_{8.0}$) was found to consist of two reactions of mass-transfer inversion of pentlandite ($\text{Fe}_{3.0}\text{Ni}_{6.0}\text{S}_{7.85}$, 46.59 at.% S) at temperatures from 586° to 600°C and a pseudoperitectoid reaction for the Ni-rich extremity of pentlandite ($\text{Fe}_{3.0}\text{Ni}_{6.0}\text{S}_{7.87}$, 46.71 at.% S) at 594°C on the $\text{Fe}_{3.0}\text{Ni}_{6.0}\text{-S}$ join in this study. On the other hand, the non-mass-transfer inversion of pentlandite ($\text{Fe}_{2.5}\text{Ni}_{6.5}\text{S}_{8.0}$) 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, 38.53 Ni and 46.65 S in at.% due to a pseudoperitectoid reaction between monosulfide solid-solution and high-form pentlandite at this temperature on the $\text{Fe}_{2.5}\text{Ni}_{6.5}\text{-S}$ 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 ($\text{Fe}_{4.5}\text{Ni}_{4.5}\text{S}_8$) 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

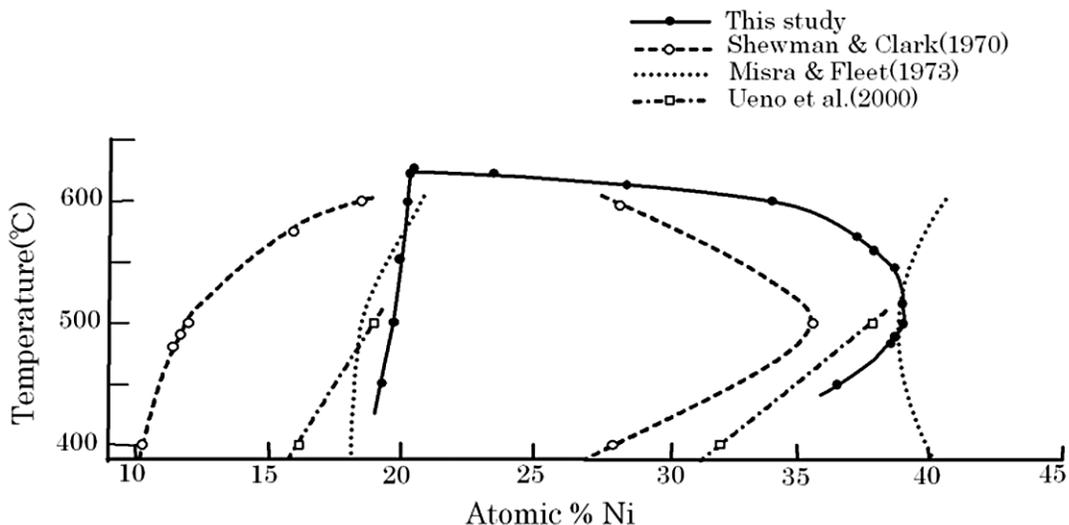


FIG. 12. A composition range in the maximum and minimum values of the Ni content of pentlandite solid-solution at temperatures from 625° to 400°C, in comparison to that proposed by Shewman & Clark (1970), Misra & Fleet (1973) and Ueno *et al.* (2000).

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 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 pseudoeutectic) 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 β_1 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 β_1) 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 ($\text{Fe}_{1.04}\text{Ni}_{7.96}\text{S}_{6.93}$) breaking down to the Ni-rich extremity of pentlandite, (high-form godlevskite and β_1) at 503, (**i** in Fig. 11) and 11) a eutectoid of β_1 ($\text{Fe}_{0.26}\text{Ni}_{2.86}\text{S}_{2.00}$) 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 is 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 divariant 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)₆Ni₃S₈], Y [CuFe₆Ni₂S₈] and Z [Cu₂Fe₅Ni₂S₈], 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 $\text{Cu}(\text{Fe},\text{Ni})_8\text{S}_8$ for phase Y (Kitakaze 2008a), and horomanite $(\text{Fe},\text{Ni},\text{Co},\text{Cu})_9\text{S}_8$ and samaniite $\text{Cu}_2(\text{Fe},\text{Ni})_7\text{S}_8$ for phases X and Z (Kitakaze 2008b, Kitakaze *et al.* 2011), respectively. Peregoedova & Ohnenstetter (2002) reported a complete quaternary solid-solution between heazlewoodite solid-solution $(\text{Ni},\text{Fe})_{3\pm x}\text{S}_2$ and intermediate solid-solution $\text{Cu}_{1\pm x}\text{Fe}_{1\pm x}\text{S}_2$ (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 Fe_9S_8 – Ni_9S_8 – Co_9S_8 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 $(\text{Fe},\text{Ni})_9\text{S}_8$ and Co_9S_8 at temperatures of 700°C, below 610°C and from 600° to 300°C, respectively. Kitakaze & Sugaki (2004) reported that a continuous solid-solution between pentlandite and cobaltpentlandite in the system Fe–Ni–Co–S inverts successively to a high-form solid-solution at temperatures from 615°C for $\text{Fe}_{4.5}\text{Ni}_{4.5}\text{S}_8$ to 831°C for Co_9S_8 with increasing Co contents, and this high-form solid-solution also forms a complete solid-solution between high-form pentlandite $(\text{Fe},\text{Ni})_9\text{S}_8$ on the Fe–Ni–S plane and high-form Co_4S_3 – Co_9S_8 solid-solution (Kitakaze & Sugaki 2000) along the edge of the Co–S boundary, through the inside of a tetrahedron of the system Fe–Ni–Co–S at 850°C (Kitakaze & Sugaki 2004). Both the high- and low-form solid-solutions between high-form pentlandite $(\text{Fe},\text{Ni})_9\text{S}_8$ and cobaltpentlandite (low-form) Co_9S_8 appear as extensive phases in the quaternary system at 650°C, and a limited zone, from about 8 to 24 mole % Co_9S_8 , of coexisting high- and low-form solid-solutions between their wide fields is found as a half-way product of the phase transition (Kitakaze & Sugaki 2004). They also expected that phase β_1 $(\text{Ni},\text{Fe})_{3\pm x}\text{S}_2$ on the Fe–Ni–S face forms a continuous solid-solution with phase $(\text{Ni},\text{Co})_{3\pm x}\text{S}_2$ on the Ni–Co–S face within the tetrahedron Fe–Ni–Co–S at 500°C.

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–Co–S and Fe–Ni–Cu–S, and finally the system Fe–Ni–Co–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.

REFERENCES

- BARKER, W.W. (1983): The Fe–Ni–S system + (Co,Cu). *CSIRO, Rep.* **FP 26**.
- BARTON, P.B., JR. & SKINNER, B.J. (1979): Sulfide mineral stabilities. In *Geochemistry of Hydrothermal Ore Deposits* (second edition; H.L. Barnes, ed.). John Wiley & Sons, New York, N.Y. (278-403).
- BATEMAN, A.M. (1952): *Economic Mineral Deposits*. John Wiley & Sons, New York, N.Y. (586-591).
- BELL, P.M., ENGLAND, J.L. & KULLERUD, G. (1964): Pentlandite, pressure effect on breakdown. *Carnegie Inst. Wash., Year Book* **63**, 206-207.
- CRAIG, J.R. & KULLERUD, G. (1969): Phase relations in the Cu–Fe–Ni–S system and their application to magmatic ore deposits. In *Magmatic Ore Deposits*, a Symposium (H.D.B. Wilson, ed.). *Econ. Geol., Monogr.* **4**, 344-358.
- CRAIG, J.R. & SCOTT, S.D. (1976): Sulfide phase equilibria. In *Sulfide Mineralogy* (P.H. Ribbe, ed.). *Rev. Mineral.* **1**, C51-110.
- CRAIG, J.R. & VAUGHAN, D.J. (1981): *Ore Microscopy and Ore Petrology*. John Wiley & Sons, New York, N.Y. (152, 160, 188, 194).
- DUMPICH, G., WASSERMANN, E.F., MANN, V., KEUNE, W., MURAYAMA, S. & MIYAKO, Y. (1987): Structural and magnetic properties of $\text{Ni}_x\text{Fe}_{1-x}$ evaporated thin films. *J. Magnetism Magnetic Mater.* **67**, 55-64.
- EDWARDS, A.B. (1954): *Textures of the Ore Minerals and their Significance*. Australasian Institute of Mining and Metallurgy, Melbourne, Australia (92, 108-110, 136).
- FEDOROVA, ZH.N. & SINYAKOVA, E.F. (1993): Experimental investigation of physicochemical conditions of pentlandite formation. *Russ. J. Geol. Geophys.* **34**, 79-87.
- FLEET, M.E. (1972): The crystal structure of α - Ni_7S_6 . *Acta Crystallogr.* **B28**, 1237-1241.
- FLEET, M.E. (1977): The crystal structure of heazlewoodite and metallic bonds in sulfide minerals. *Am. Mineral.* **62**, 341-345.
- FLEET, M.E. (1987): Structure of godlevskite, Ni_9S_8 . *Acta Crystallogr.* **C43**, 2255-2257.
- FLEET, M.E. (2006): Phase equilibria at high temperatures. In *Sulfide Mineralogy and Geochemistry* (D.J. Vaughan, ed.). *Rev. Mineral.* **61**, 365-419.

- FRANCIS, C.A., FLEET, M.E., MISRA, K.C. & CRAIG, J.R. (1976): Orientation of exsolved pentlandite in nature and synthetic nickeliferous pyrrhotite. *Am. Mineral.* **61**, 913-920.
- FUJII, T., YOSHIDA, A., TANAKA, K., MARUMO, F. & NODA, Y. (1986): High pressure compressibilities of pyrite and catterite. *Mineral. J.* **13**, 202-211.
- FUTAMI, T. & ANZAI, S. (1984): Impurity effects of the 3d transition metal atoms on the first-order magnetic and electrical transition in NiS. *J. Appl. Phys.* **56**, 440-447.
- HAWLEY, J.E., ed. (1962): The Sudbury ores: their mineralogy and origin. *Can. Mineral.* **7**, 1-207.
- HAYASHI, T. (1985): *Study on the Phase Equilibrium in the System Cu–Fe–Ni–S, Especially Phase Relation in the Central Portion*. Ph.D. thesis, Tohoku University, Sendai, Japan.
- HILL, R.E.T. (1983): Experimental study of phase relations at 600°C in a portion of the Fe–Ni–Cu–S system and its application to natural sulphide assemblages. In *Sulphide Deposits in Mafic and Ultramafic Rocks* (D.L. Buchanan & M.J. Jones, eds.). The Institution of Mining and Metallurgy, London, U.K. (14-21).
- HSIEH, K.-C., CHANG, Y.A. & ZHONG, T. (1982): The Fe–Ni–S system above 700°C. *Bull. Alloy Phase Diagrams* **3**, 165-172.
- KANEDA, H., TAKENOCHI, S. & SHOJI, T. (1986): Stability of pentlandite in the Fe–Ni–Co–S system. *Mineral. Deposita* **21**, 169-180.
- KARUP-MØLLER, S. & MAKOVICKY, E. (1995): The phase system Fe–Ni–S at 725°C. *Neues Jahrb. Mineral., Monatsh.*, 1-10.
- KITAKAZE, A. (1998): Sulfide minerals from the Horoman peridotite, Hokaido, Japan. *J. Japan. Assoc. Mineral. Petrol. Econ. Geol.* **93**, 369-379 (in Japanese with English abstr.).
- KITAKAZE, A. (2008a): Sugakiite, $\text{Cu}(\text{Fe,Ni})_8\text{S}_8$, a new mineral species from Hokkaido, Japan. *Can. Mineral.* **46**, 263-267.
- KITAKAZE, A. (2008b): Horomanite, $(\text{Fe,Ni,Co,Cu})_9\text{S}_8$, and samaniite, $\text{Cu}_2(\text{Fe,Ni})_7\text{S}_8$, new mineral species from Horoman peridotite massif, Hokkaido, Japan. *Collected Abstract 2008, Japan Assoc. Mineral. Sci. (Akita)*, 123 (abstr.).
- KITAKAZE, A., ITOH, H. & KOMATSU, R. (2011): Horomannite, $(\text{Fe,Ni,Co,Cu})_9\text{S}_8$, and samaniite, $\text{Cu}_2(\text{Fe,Ni})_7\text{S}_8$, new mineral species from the Horoman peridotite massif, Hokkaido, Japan. *J. Mineral. Petrol. Sci.* **106**, 204-210.
- KITAKAZE, A. & SUGAKI, A. (1996): Study of phase $\text{Ni}_{3\pm x}\text{S}_2$ in the Ni–S system, especially high-temperature forms of Ni_3S_2 and Ni_4S_3 . *Joint Annual Meeting Japan. Assoc. Mineral., Petrol. Econ. Geol., Mineral. Soc. Japan & Soc. Resource Geol. (Kanazawa)*, 149 (abstr.).
- KITAKAZE, A. & SUGAKI, A. (2000): The phase relations in a metal-rich portion of the Co–S system above 700°C, especially reexamination of phase Co_4S_3 . *Joint Annual Meeting Mineral. Soc. Japan & Assoc. Mineral. Petrol. Econ. Geol. (Sendai)*, 48 (abstr.).
- KITAKAZE, A. & SUGAKI, A. (2001): Study of phase $\text{Ni}_{3\pm x}\text{S}_2$ in the Ni–S system with emphasis on the phases of high-form Ni_3S_2 (β_1), and Ni_4S_3 (β_2). *Neues Jahrb. Mineral., Monatsh.*, 41-48.
- KITAKAZE, A. & SUGAKI, A. (2004): The phase relations between $\text{Fe}_{4.5}\text{Ni}_{4.5}\text{S}_8$ and Co_9S_8 in the system Fe–Ni–Co–S at temperatures from 400 to 1100°C. *Can. Mineral.* **42**, 17-42.
- KNOP, O. & IBRAHIM, M.A. (1961): Chalkogenides of the transition elements. II. Existence of the π phase in the M_9S_8 section of the system Fe–Co–Ni–S. *Can. J. Chem.* **39**, 297-317.
- KOJONEN, K. (1976): Experiments on synthetic pentlandite. In *Ore Mineral Systems* (G.H. Moh, ed.). *Neues Jahrb. Mineral., Abh.* **126**, 133-135.
- KOSYAKOV, V.I., KRAEVA, A.G., FEODROVA, Z.N. & SINYAKOVA, E.F. (1996): Topological analysis of evolution of phase equilibria in the Fe–Ni–S system in the range ≤ 0.5 along the temperature axis. *Russ. J. Geol. Geophys.* **37**, 5-15.
- KUBASCHEWSKI, O. (1982): *Iron – Binary Phase Diagrams*. Springer-Verlag, New York, N.Y.
- KULLERUD, G. (1962): The Fe–Ni–S system. *Carnegie Inst. Wash., Yearbook* **61**, 144-150.
- KULLERUD, G. (1963a): Thermal stability of pentlandite. *Can. Mineral.* **7**, 353-366.
- KULLERUD, G. (1963b): The Fe–Ni–S system. *Carnegie Inst. Wash., Yearbook* **62**, 175-189.
- KULLERUD, G. & YUND, R.A. (1962): The Ni–S system and related minerals. *J. Petrol.* **3**, 126-175.
- KULLERUD, G., YUND, R.A. & MOH, G.H. (1969): Phase relations in the Cu–Fe–S, Cu–Ni–S, and Fe–Ni–S systems. In *Magmatic Ore Deposits* (H.D.B. Wilson, ed.). *Econ. Geol., Monogr.* **4**, 323-343.
- LIN, R.Y., HU, D.C. & CHANG, Y.A. (1978): Thermodynamics and phase relationships of transition metal sulfur systems. II. The nickel–sulfur system. *Metall. Trans.* **9B**, 531-538.
- LINÉ, G. & HUBER, M. (1963): Étude radiocristallographique à haute température de la phase non stoechiométrique $\text{Ni}_{3\pm x}\text{S}_2$. *C.R. Acad. Sci.* **256**, 3118-3120.
- LINDGREN, W. (1933): *Mineral Deposits*. McGraw-Hill Book Co., New York, N.Y.
- LINDGREN, W. (1937): Succession of minerals and temperatures of formation in ore deposits of magmatic affiliation. *Trans. Am. Inst. Mining & Metall. Eng.* **126**, 356-376.

- LINDQVIST, M., LINDQVIST, D. & WESTGREN, A. (1936): The crystal structure of Co_9S_8 and of pentlandite $(\text{Fe,Ni})_9\text{S}_8$. *Kemisk Tidskr.* **48**, 156-160.
- LUTTS, A. & GIELEN, P.M. (1970): The order-disorder transformation in FeNi_3 . *Physica Status Solidi* **41**, K81-K84.
- MISRA, K.C. & FLEET, M.E. (1973a): The chemical compositions of synthetic and natural pentlandite assemblages. *Econ. Geol.* **68**, 518-539.
- MISRA, K.C. & FLEET, M.E. (1973b): Unit cell parameters of monosulfide, pentlandite and taenite solid solutions within the Fe-Ni-S system. *Mater. Res. Bull.* **8**, 669-677.
- NALDRETT, A.J., CRAIG, J.R. & KULLERUD, G. (1967): The central portion of the Fe-Ni-S system and its bearing on pentlandite exsolution in iron-nickel sulfide ores. *Econ. Geol.* **62**, 826-847.
- NOWACKI, E., SCHWARZENBACH, D. & HAHN, T. (1991): Charge densities in CoS_2 and NiS_2 (pyrite structure). *Acta Crystallogr.* **B47**, 650-659.
- PARK, C.F. & MACDIARMID, R.A. (1964): *Ore Deposits*. W.H. Freeman and Co., San Francisco, California.
- PEREGOEDOVA, A. & OHNENSTETTER, M. (2002): Collectors of Pt, Pd and Rh in a S-poor Fe-Ni-Cu sulfide system at 760°C: experimental data and application to ore deposits. *Can. Mineral.* **40**, 527-561.
- RAJAMANI, V. & PREWITT, C.T. (1973): Crystal chemistry of natural pentlandites. *Can. Mineral.* **12**, 178-187.
- RAMDOHR, P. (1980): *The Ore Minerals and Their Intergrowths* 2. Pergamon Press, Oxford, U.K.
- RAMSDEN, A.R. & CAMERON, E.N. (1966): Kamacite and taenite superstructures and a metastable tetragonal phase in iron meteorites. *Am. Mineral.* **51**, 37-55.
- RAU, H. (1976): Homogeneity range of high temperature $\text{Ni}_{3\pm x}\text{S}_2$. *J. Phys. Chem. Solids* **37**, 929-930.
- ROSENQVIST, T. (1954): A thermodynamic study of the iron, cobalt, and nickel sulphides. *J. Iron Steel Inst.* **176**, 37-57.
- SACK, R.O. & EBEL, D.S. (2006): Thermochemistry of sulfide mineral solutions. In *Sulfide Mineralogy and Geochemistry* (D.J. Vaughan, ed.). *Rev. Mineral.* **61**, 265-364.
- SHARMA, R.C. & CHANG, Y.A. (1980): Thermodynamics and phase relationships of transition metal-sulfur systems. IV. Thermodynamic properties of the Ni-S liquid phase and the calculation of the Ni-S phase diagram. *Metall. Trans.* **11B**, 139-146.
- SHEWMAN, R.W. & CLARK, L.A. (1970): Pentlandite phase relations in the Fe-Ni-S system and notes on the monosulfide solid solution. *Can. J. Earth Sci.* **7**, 67-85.
- SINGLETON, S., NASH, P. & LEE, K.J. (1991): Ni-S. In *Binary Alloy Phase Diagrams* **2** (T.B. Massalski, J.L. Murray, L.H. Bennett & H. Baker, eds.). American Society of Metals, Metal Park, Ohio.
- SINYAKOVA, E.F. & KOSYAKOV, V.I. (2001): 600°C section of the Fe-FeS-NiS-Ni phase diagram. *Inorg. Mater.* **37**, 1130-1137.
- SUGAKI, A. & KITAKAZE, A. (1990): Hydrothermal synthesis of pentlandite. In *Dynamic Processes of Material Transport and Transformation in the Earth Interior* (F. Marumo, ed.). Terra Scientific Publishing Co., Tokyo, Japan (113-117).
- SUGAKI, A. & KITAKAZE, A. (1992): Phase transition of pentlandite. *Proc. 29th Int. Geol. Congress (Kyoto)* **3**, 676 (abstr.).
- SUGAKI, A. & KITAKAZE, A. (1996): New data of high-pentlandite solid solution study on the Fe-Ni-S system (5). *Joint Annual Meeting, Japan. Assoc. Mineral. & Econ. Geol., Mineral. Soc. Japan, Soc. Resource Geol. (Kanazawa)*, 150 (abstr.).
- SUGAKI, A. & KITAKAZE, A. (1998): High form of pentlandite and its thermal stability. *Am. Mineral.* **83**, 133-140.
- SUGAKI, A. & KITAKAZE, A. (2006): New phase relations of the system Fe-Ni-S at temperatures from 875° to 450°C as the pentlandite ore genesis. *Int. Mineral. Assoc., 19th Gen. Meeting (Kobe), Program Abstr.*, 197.
- SUGAKI, A., KITAKAZE, A. & HAYASHI, T. (1982): High-temperature phase of pentlandite. *Mineral. Soc. Japan, Annual Meeting (30th anniv., Tsukuba)* **P-22**, 60 (abstr., in Japanese).
- SUGAKI, A., KITAKAZE, A. & HAYASHI, T. (1983): New data on pentlandite stability. *Mining Geol.* **33**, 63 (abstr., in Japanese).
- SUGAKI, A. & KITAKAZE, A. & HAYASHI, T. (1984): The solid solution of pentlandite and its phase relations at temperatures from 600 to 800°C. *J. Japan. Assoc. Mineral., Petrol. Econ. Geol.* **79**, 175-176 (abstr., in Japanese).
- SUGAKI, A., SHIMA, H. & KITAKAZE, A. (1976): Application of Bence and Albee method to sulfide minerals: the Cu-Fe-Pb-Bi-S system. *J. Mineral. Soc. Japan* **12** (special issue), 85-92 (in Japanese).
- SWARTZENDRUBER, L.J., ITKIN, V.P. & ALCOCK, C.B. (1993): Fe-Ni (iron-nickel) system. In *Phase Diagrams of Binary Iron Alloys* (H. Okamoto, ed.). The Materials Information Society, Materials Park, Ohio (256-278).
- UENO, T., ITO, S., NAKATATSUKA, S., NAKANO, K., HARADA, T. & YAMAZAKI, T. (2000): Phase equilibria in the system Fe-Ni-S at 500° and 400°C. *J. Mineral. Petrol. Sci.* **95**, 145-161.

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