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

Arashi KITAKAZE[§]

Museum of Sugaki Ore Collection, Yamaguchi University, 2-16-1 Tokiwadai, Ube 755-8611, Japan

Takaaki MACHIDA and Ryuichi KOMATSU

Graduate School of Science and Engineering, Yamaguchi University, 2-16-1 Tokiwadai, Ube 755-8611, Japan

Abstract

High-form pentlandite of composition $Fe_{4.93}Ni_{4.06}S_{8.01}$ first crystallizes by peritectic reaction between liquid and monosulfide solid-solution at 870 ± 3 °C (865 ± 3 °C for high-form pentlandite with Fe=Ni in at.%) in the Fe–Ni–S system; it forms a limited solid-solution from $Fe_{5.08}Ni_{3.93}S_{7.99}$ to $Fe_{3.81}Ni_{5.24}S_{7.96}$ including the ideal composition $Fe_{4.50}Ni_{4.50}S_{8.00}$ at 850 °C. The solid solution grows rapidly to extend its field toward the Ni-rich side with decreasing temperature and connects with β_2 (44.7 at.% S) in the Ni–S join at 806 ± 3 °C (peritectic between liquid and $Ni_{1-x}S$). Below the peritectic temperature, high-form pentlandite (metal-rich composition) crystallizes directly from liquid. This crystallization continues to the eutectic (746 ± 3 °C for the high form with Fe=Ni) with decreasing temperature, and the high-form solid solution grows still more. Crystallization of the monosulfide solid-solution and high-form pentlandite solid solution from liquid finishes at 762 ± 3 °C and 739 ± 3 °C, respectively. The high-form pentlandite solid solution extended from the Ni–S join is maintained at 700 and 650 °C and coexists with monosulfide solid-solution and/or with liquid (870 to 739 °C), and/or with β_1 or its solid solution (800 to 503 °C), and/or with γ (762 to 579 °C).

In geological processes such as the formation of Ni-Cu ore deposits, pentlandite can crystallize as the high form from liquid (sulfide magma) by peritectic and eutectic reactions at comparatively high temperatures from 870 to 739 °C (Fe–Ni–S system). Pentlandite is also produced by the breakdown of the high form at the pseudoeutectoid (or ternary eutectoid). Pentlandite can further be formed by exsolution from monosulfide solid-solution below 600 °C, and from the ternary β_1 phase.

Keywords: Fe–Ni–S system, high-form pentlandite, pentlandite, monosulfide solid-solution, β_1 solid-solution.

Introduction

This paper continues from our previous paper (Kitakaze *et al*. 2011) on the Fe–Ni–S system from 650 to 450 °C; results regarding phase relations from 875 to 650 °C are the main topic. Since the study by Kullerud (1962, 1963a), it has been assumed that pentlandite ($Fe_{4.5}Ni_{4.5}S_{8.0}$) is present as a stable phase below 610 ± 3 °C and breaks down to a mixture of $Ni_{3\pm x}S_2$ and pyrrhotite (monosulfide solid-solution) at or above this temperature (Kullerud *et al*. 1969, Craig & Scott 1976, Kosyakov & Sinyakova 2006). However, Sugaki *et al*. (1983, 1984) and Kitakaze *et al*. (2011) found that pentlandite (Fe=Ni in at.%) does not break down at this temperature, but transforms into a higher form, which is stable up to 865 ± 3 °C. The

high-form pentlandite is unquenchable and always shows the X-ray pattern for pentlandite (low form) at room temperature. Sugaki & Kitakaze (1992, 1998) and Kitakaze *et al*. (2011) verified using high-temperature X-ray diffraction that the high form ($Fe_{4.50}Ni_{4.50}S_{7.80}$) has a primitive cubic cell with $a = 5.189$ Å (620 °C), corresponding to one-half of the cell edge of pentlandite. The high-low inversion is reversible, and might be an order-disorder (perhaps defect sphalerite structure) transformation.

Sugaki *et al*. (1983, 1984) also found that high-form pentlandite appears as an extensive solid solution from a more Fe-rich composition than $Fe_{4.5}Ni_{4.5}S_{8.0}$ to $Ni_{3\pm x}S_2$ on the Ni–S boundary of the Fe–Ni–S system at 800 and 650 °C. Hayashi (1985) recognized the existence of the same solid solution in the quaternary

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[§] *Corresponding author e-mail address*: kitakaze@yamaguchi-u.ac.jp

Cu–Fe–Ni–S at 850 and 650 °C. Fedorova & Sinyakova (1993) and Karup-Møller & Makovicky (1995) reported an extended heazlewoodite solid-solution $(Fe_xNi_{1-x})_{3\pm y}S_2$ at 820 and 600 °C and an elongated $(Ni,Fe)_{3\pm x}S_2$ solid-solution at 725 °C, respectively, using the terminology of the authors. Both phases correspond to the high-form pentlandite – $Ni_{3\pm x}S_2$ solid-solution of Sugaki *et al.* (1983, 1984) and Kitakaze *et al.* (2011).

On the other hand, Lin *et al.* (1978), Sharma & Change (1980), Singleton *et al.* (1991), and Kitakaze & Sugaki (2001) found that $Ni_{3\pm x}S_2$ (β) in binary Ni–S is not a monophase, but consists of two limited solid-solutions of phases β_1 (Ni_3S_2, corresponding to high-form heazlewoodite) and β_2 (Ni_4S_3, a high-temperature phase) with a narrow immiscibility field between them, over the temperature range from 524 to 806 °C, using a gas equilibration technique. Sugaki & Kitakaze (1996), Kitakaze & Sugaki (2001), and Kitakaze *et al.* (2011) ascertained crystallographically the existence of phases β_1 and β_2 in the $Ni_{3\pm x}S_2$ field using high-temperature X-ray diffraction techniques.

The appearance of high-form pentlandite β_1 solid-solution and β_2 as stable phases required the reexamination and revision of the phase diagrams of the system Fe–Ni–S above 650 °C as shown by previous authors (Kullerud 1963b, Kullerud *et al.* 1969, Hsieh *et al.* 1982, Baker 1983, Hayashi 1985, Fedorova & Sinyakova 1993, Karup-Møller & Makovicky 1995, Peregoedova & Ohnensetter 2002). Thus, we investigated the isotherms at temperatures from 875 to 650 °C. In this paper, we present new experimental data in the Fe–Ni–S system, especially phase relations with high- and low-form pentlandites, β_1 and β_2, above 650 °C and their thermal stabilities.

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

EXPERIMENTAL PROCEDURE

Synthesis and equilibrium experiments

The syntheses were carried out by the evacuated silica-glass tube method. The starting materials, Fe (99.999%) and Ni (99.999%) from Johnson Matthey Co. Ltd. and S (99.99%) from Kanto Chemical Co. Ltd., were weighed for the desired composition of each experiment, and then sealed in transparent silica-glass tubes under a vacuum of 1.33×10^{-1} Pa (10^{-3} torr).

The sealed tubes with their charges were kept at 850, 800, 750, 700, and 650 °C for 10 days. The products were ground and mixed under acetone in an evacuated silica tube and reheated at 850, 800, 750, 700, and 650 °C for at least 3, 5, 15, 30, and 40 days,

respectively. After reheating, the tubes were rapidly cooled in ice water. The final products were aggregates of fine anhedral grains, 20 to 100 μm in size, except for S and sulfide liquids.

Microscopic examination

All the experimental products were examined with a reflected light microscope. Among the products, pyrite, vaesite, monosulfide solid-solution, and metals of α ("kamacite" = iron) and γ (taenite) compositions were the homogeneous phases after quenching. However, high-form pentlandite-β_1 solid solution, β_2, and sulfide liquid were not present as mono-phases after quenching, and the products consisted of cooling products that appeared as consequences of phase transformation, eutectic, eutectoid, peritectic, peritectoid, or exsolution reactions. Because the experimental products composed of low-form pentlandite, godlevskite, heazlewoodite, monosulfide solid-solution, and metal phases have small grain sizes, backscattered electron (BSE) images, obtained with an electron-probe microanalyzer (EPMA), were generally used in addition to examination with a reflected light microscope.

X-ray powder diffraction

Because high-form pentlandite-β_1 solid-solution and the β_2 phase are unquenchable, X-ray powder diffractometers (JEOL JDX-7S and Rigaku Geigerflex RAD-C) with high-temperature heating units (JEOL DX-GOH V2 and Rigaku CN2311B1) were used for identification of these phases using the method described by Kitakaze *et al.* (2011).

Electron probe microanalysis

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

Nickel-rich high-form pentlandite and β_2 have similar compositions and are accompanied by cooling products such as low pentlandite, monosulfide solid-solution, godlevskite, heazlewoodite, and metal phases. The phase assemblages were confirmed by high-temperature X-ray diffraction for each temperature. In reference to these results, bulk compositions were obtained by analysis with a larger beam diameter (20~40 μm) and by averaging values for 10 to 15 point analysis.

TABLE 1. CHEMICAL COMPOSITIONS AND CRYSTALLOGRAPHIC DATA FOR MINERALS AND PHASES APPEARING IN THIS STUDY

Minerals and phases	Symbols	Compositions	Structure types Cell edges in Å	References
Pyrite	py	$(Fe,Ni)S_2$	Cubic $Pa3$ a 5.3825	Fujii *et al.* (1986)
Vaesite	vs	$(Ni,Fe)S_2$	Cubic $Pa3$ a 5.6765	Nowack *et al.* (1991)
Monosulfide solid-solution	mss	$(Fe,Ni)_{1-x}S$ $(Fe=Ni)$	Hexagonal $P6_3/mmc$ a 3.45, c 5.6	Craig & Scott (1976)
High-form pentlandite	hpn	$(Fe,Ni)_9S_8$ $(Fe=Ni)$	Cubic $Pn3m$ a 5.245(650 °C)	Sugaki & Kitakaze (1998)
Pentlandite	pn	$(Fe,Ni)_9S_8$ $(Fe=Ni)$	Cubic $Fm3m$ a 10.100	Rajamani & Prewitt (1973) Sugaki & Kitakaze (1998)
Phase β_2	β_2	$Ni_4S_3(SS)$	Cubic $Pn3m$ a 5.140(600 °C)	Kitakaze & Sugaki (2001)
Phase β_1	β_1	$Ni_3S_2(SS)$	Cubic $Fm3m$ a 5.210(600 °C)	Kitakaze & Sugaki (2001)
Phase α ("kamacite")	α	(Fe,Ni) $Fe_{0.96}Ni_{0.06}$	Cubic $Fm3m$ a 2.860	Ramsden & Cameron (1966)
Phase γ (taenite)	γ	(Fe,Ni) $Fe_{0.30}Ni_{0.70}$	Cubic $Fm3m$ a 3.587	Dumpich *et al.* (1987)

Note: SS = solid-solution.

Standard deviation of the analytical values obtained by EPMA were as follows: (1) ±0.1 wt.% for Fe, Ni, and S of a monophase without quench products, such as pyrite, vaesite, pentlandite, and monosulfide solid-solution; (2) ±0.3 wt.% for Fe, Ni, and S in the phases with quenching products, such as high-form pentlandite solid solution, β_2, and liquid.

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

Differential thermal analysis (DTA)

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

EXPERIMENTAL RESULTS

Phase relations at 875 °C

Phase relations in the Fe–Ni–S system at 875 °C were obtained from the equilibrium experimental data and the EPMA data for the synthetic products, and are shown in Figure 1. Only six phases appeared at this temperature: four solid phases, *e.g.*, vaesite, monosulfide solid-solution, α, and γ, and two liquid phases, *e.g.*, sulfide and sulfur. Monosulfide solid solution appears as the first sulfide phase, $Fe_{1-x}S$ ($Fe_{0.92}S_{1.00}$), in the system at 1188 °C (Rau 1975, Kubaschewski 1982, Okamoto 1990), extends its field successively in the NiS direction with decreasing temperature, and forms a complete solid solution between $Fe_{1-x}S$ (1C) and $Ni_{1-x}S$ below 999 ± 3 °C, at which temperature $Ni_{1-x}S$ melts congruently (Kullerud & Yund 1962, Arnold & Malik 1975, Rau 1975, Lin *et al.* 1978, Sharma & Chang 1980, Singleton *et al.* 1991). Vaesite, which crystallized as the stable phase NiS_2 *via* a synthetic reaction between two immiscible liquids, Ni-rich liquid and sulfur liquid, at 1022 ± 3 °C (Arnold & Malik 1975, Lin *et al.* 1978, Sharma & Chang 1980, Singleton *et al.* 1991), has a limited solid-solution ranging from NiS_2 to $Fe_{0.18}Ni_{0.82}S_{2.00}$ along the FeS_2–NiS_2 join at 875 °C. The sulfide liquid phase occupies a wide field extending from the Ni–S join toward the inside of the ternary up to $Fe_{0.43}Ni_{0.17}S_{0.41}$.

In the figure, three univariant assembles are found, as follows: (1) vaesite ($Fe_{0.13}Ni_{0.86}S_{2.00}$) + monosulfide solid-solution ($Fe_{0.23}Ni_{0.58}S_{1.00}$) + S (liquid); (2) monosulfide ($Fe_{0.89}Ni_{0.11}S_{1.00}$) + liquid ($Fe_{0.43}Ni_{0.17}S_{0.41}$) + γ ($Fe_{0.54}Ni_{0.46}$), and (3) monosulfide solid-solution ($Fe_{0.94}Ni_{0.06}S_{1.00}$) + α ($Fe_{0.99}Ni_{0.01}$) + γ($Fe_{0.97}Ni_{0.03}$).
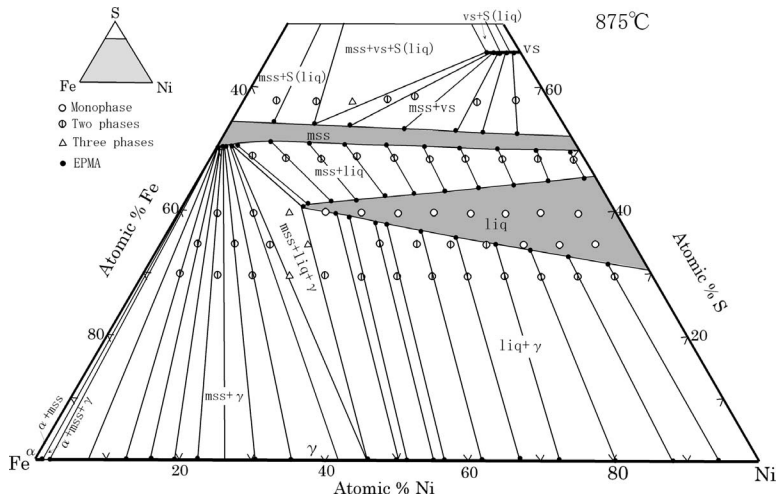
FIG. 1. The phase diagram in the Fe–Ni–S system at 875 °C in the presence of an equilibrium vapor. Abbreviations: See Table 1; liq = liquid, S(l) = sulfur liquid.

Phase relations from 875 to 850 °C

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

Phase relations at 850 °C

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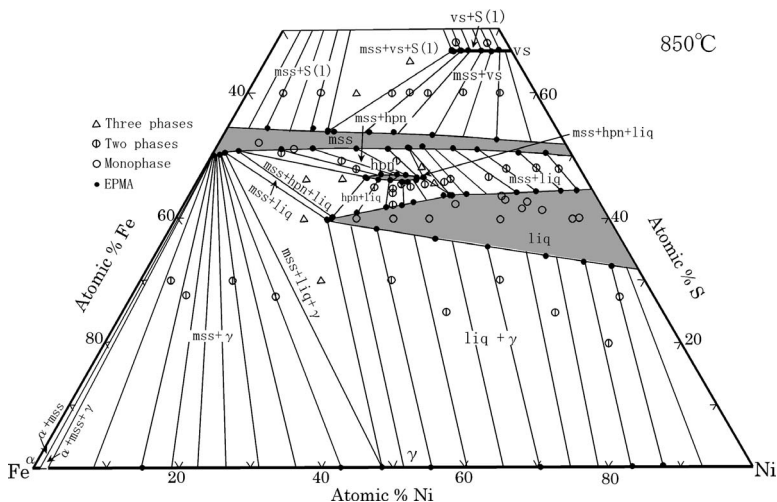

FIG. 2. The phase diagram in the Fe–Ni–S system at 850 °C in the presence of an equilibrium vapor. Abbreviations: See Table 1; liq = liquid, S(l) = sulfur liquid.
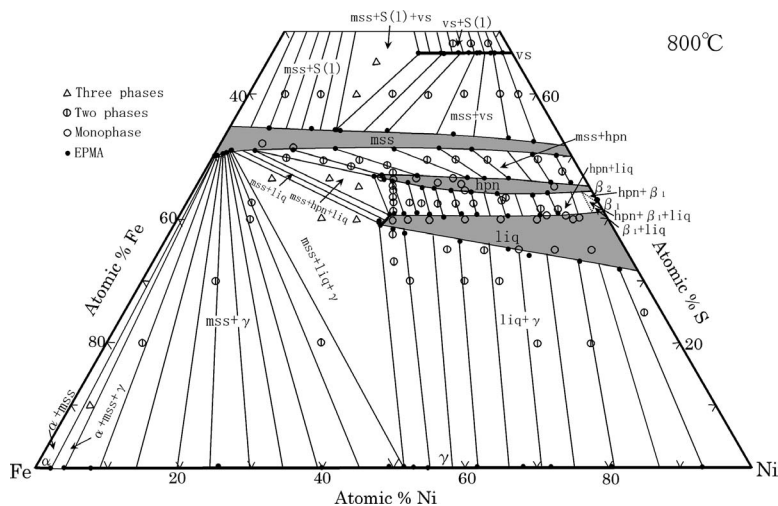
Fig. 3. The phase relations in the Fe–Ni–S system at 800 °C in the presence of an equilibrium vapor. Abbreviations: See Table 1, but hpn shows a continuous SS from high-form pentlandite to phase β_2 of the Ni–S join.

join toward the inside of the ternary up to $Fe_{0.38}Ni_{0.22}S_{0.40}$. The high-form pentlandite solid solution coexists with monosulfide solid solution and/or liquid. The α ($Fe_{0.99}Ni_{0.01}$) phase coexists with γ ($Fe_{0.98}Ni_{0.02}$) (Kubaschewski 1982, Swartzendruber *et al*. 1993) and monosulfide solid-solution.

Two univariant assemblages were found as follows: (1) high-form pentlandite ($Fe_{5.08}Ni_{3.93}S_{7.99}$) + monosulfide solid-solution ($Fe_{0.87}Ni_{0.12}S_{1.00}$) + γ ($Fe_{0.51}Ni_{0.49}$); and (2) high-form pentlandite ($Fe_{3.81}Ni_{5.24}S_{7.96}$) + monosulfide solid-solution ($Fe_{0.44}Ni_{0.53}S_{1.00}$) + liquid ($Fe_{0.39}Ni_{0.21}S_{0.40}$) in the metal-rich portion. The high-form pentlandite solid solution can't coexist with γ because of the existence of an extensive liquid field. The liquid ($Fe_{0.40}Ni_{0.22}S_{0.38}$) on the metal-rich side coexists with monosulfide solid solution ($Fe_{0.95}Ni_{0.04}S_{1.00}$) and γ ($Fe_{0.52}Ni_{0.48}$) as a univariant assemblage. Most Fe-rich monosulfide solid solution ($\sim$FeS) can coexist with α ($Fe_{0.99}Ni_{0.01}$) and γ ($Fe_{0.98}Ni_{0.02}$) as a univariant assemblage.

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

The phase relations of the metal-rich portions at 850 °C are similar to those noted at 820 °C by Fedorova & Sinyakova (1993). However, the field for high-form pentlandite solid solution is more S-rich than that of the heazlewoodite solid solution. The Fe-rich ends of the high-form pentlandite and liquid are more Fe-rich by then.

Phase relations at 800 °C

The phase relations at 800 °C were obtained from the equilibrium experiment and the EPMA data and are shown in Figure 3. The field for the high-form pentlandite solid solution extends rapidly toward the Ni-rich side with decreasing temperature below 850 °C, and reaches the Fe-free β_2 (44.7 at.% S) point in the Ni–S join at 806 ± 3 °C, at which temperature β_2 crystallizes (Lin *et al*. 1978). As seen in the Figure, a continuous solid solution from high-form pentlandite to β_2 exists at 800 °C. The Fe-rich end composition of the solid solution ($Fe_{5.29}Ni_{3.74}S_{7.97}$) at 800 °C contains slightly more Fe than that at 850 °C. Phase β_1 with the S-richest composition ($\sim$42.9 at.% S) appears by peritectic reaction between β_2 and liquid in the Ni–S join at 800 °C. The liquid phase still occupies an extensive field, but it retreats toward the Ni–S join at 800 °C. The continuous monosulfide solid solution is present as at 850 °C, but it cannot coexist with the liquid phase, except the Fe-rich portion, because of the intervening continuous solid solution of high-form pentlandite–β_2 at 800 °C. The high-form pentlandite–β_2 solid solution (hereafter referred to as high-form pentlandite solid solution) coexists with the monosulfide solid solution and/or liquid. However, it cannot yet coexist with γ due to the existence of the intervening liquid field. The monosulfide solid solution near FeS coexists with α and Fe-rich γ, while the metal-rich liquid coexists with Ni-rich γ.

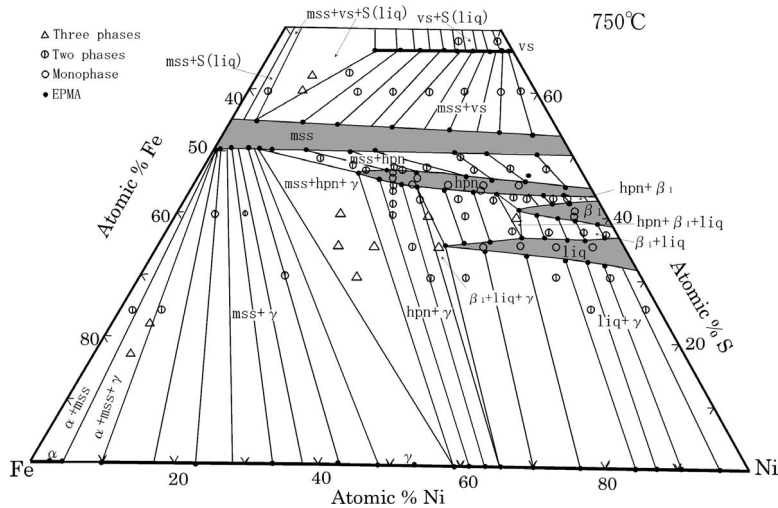Five univariant assemblages are found in the isotherm at 800 °C as follows: (1) high-form

F IG. 4. The phase relations in the Fe–Ni–S system at 750 °C in the presence of an equilibrium vapor. Abbreviations: See Table 1, but hpn shows a continuous SS from high-form pentlandite to phase β_2 of the Ni–S join, and β_1 has wide range of solid solutions.

pentlandite ($Fe_{5.29}Ni_{3.74}S_{7.97}$) + monosulfide solid solution ($Fe_{0.87}Ni_{0.12}S_{1.00}$) + liquid ($Fe_{0.31}Ni_{0.29}S_{0.41}$); (2) monosulfide solid solution ($Fe_{0.94}Ni_{0.04}S_{1.00}$) + liquid ($Fe_{0.30}Ni_{0.33}S_{0.38}$) + γ ($Fe_{0.48}Ni_{0.52}$); (3) mono-sulfide solid solution ($Fe_{0.99}Ni_{0.01}S_{1.00}$) + α ($Fe_{0.98}Ni_{0.02}$) + γ ($Fe_{0.96}Ni_{0.04}$) (Kubaschewski 1982); (4) β_1 (42.9 at.% S) + high-form pentlandite + liquid; and (5) vaesite ($Fe_{0.40}Ni_{0.60}S_{2.00}$) + monosulfide solid solution ($Fe_{0.62}Ni_{0.19}S_{1.00}$) + S(liquid).

Phase relations from 800 to 750 °C

On cooling from 800 °C, the liquid phase retreats further toward the Ni-rich side. The tie-lines between monosulfide solid solution and liquid are replaced by those between high-form pentlandite and γ at 762 ± 3 °C (invariant). This tie-line change was ascertained by DTA (2 °C/min heating rate), microscopic examina-tion, and EPMA data. The reaction is reversible.

Below 762 ± 3 °C monosulfide solid solution cannot crystallize from liquid *via* a pseudoeutectic reaction. Phase β_1 grows and quickly extends as a solid solution from the Ni–S join within the ternary field with decreasing temperature, forming a solid solution with a fairly large area.

Phase relation at 750 °C

The phase relation determined from the data for equilibrium studies and EPMA at 750 °C is shown in Figure 4. There are five univariant assemblages in the system as follows: (1) monosulfide solid solution ($Fe_{0.86}Ni_{0.13}S_{1.00}$) + high-form pentlandite ($Fe_{5.44}$

$Ni_{3.60}S_{7.96}$) + γ ($Fe_{0.42}Ni_{0.56}$); (2) high-form pentland-ite ($Fe_{4.20}Ni_{5.32}S_{7.48}$) + liquid ($Fe_{0.20}Ni_{0.44}S_{0.36}$) + γ ($Fe_{0.34}Ni_{0.66}$); (3) high-form pentlandite ($Fe_{2.35}Ni_{7.21}$ $S_{7.45}$) + β_1 ($Fe_{0.55}Ni_{2.34}S_{2.00}$) + liquid ($Fe_{0.14}Ni_{0.50}$ $S_{0.37}$); (4) monosulfide solid solution ($Fe_{0.97}Ni_{0.03}$ $S_{1.00}$) + α ($Fe_{0.95}Ni_{0.05}$) + γ ($Fe_{0.90}Ni_{0.10}$); (5) monosulfide solid solution ($Fe_{0.72}Ni_{0.10}S_{1.00}$) + vaesite ($Fe_{0.59}Ni_{0.41}S_{2.00}$) + S (liquid).

Relation from 750 to 700 °C

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

Other tie-line changes from high-form pentlandite and liquid to β_1 and γ at 739 ± 3 °C were ascertained by DTA, microscopic examination, and EPMA. The compositions of the four coexisting phases were estimated to be $Fe_{3.03}Ni_{6.41}S_{7.57}$ for high-form pent-landite, $Fe_{0.78}Ni_{2.10}S_{2.00}$ for β_1, $Fe_{0.17}Ni_{0.48}S_{0.35}$ for liquid, and $Fe_{0.25}Ni_{0.75}$ for γ as the invariant association. Below this temperature, no crystallization of high-form pentlandite from liquid as pseudoeutectic is found.

Phase relations at 700 °C

The isothermal phase diagram at 700 °C, obtained from the equilibrium experimental and EPMA data for the phases produced, is shown in Figure 5. High-form pentlandite continues as an elongated solid-solution from $Fe_{5.07}Ni_{4.03}S_{7.90}$ to phase β_2 in the Ni–S join (~43.0–44.5 at.% S). The liquid field shrinks toward the Ni-rich side, but persists as a small field reaching
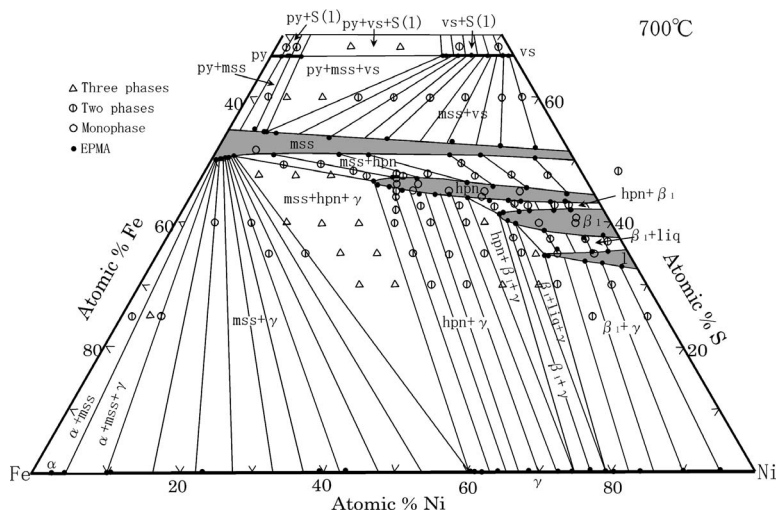
FIG. 5. The isothermal diagram in the Fe–Ni–S system at 700 °C in the presence of an equilibrium vapor. Abbreviations: See Table 1.

the Ni–S join. The Fe-rich portion of the metal-rich side of the high-form pentlandite solid solution coexists with γ, whereas its Ni-rich portion coexists with $β_1$ solid solution. On the other hand, metal-rich $β_1$ solid solution coexists with S-rich liquid, whereas metal-rich liquid coexists with Ni-rich γ. Monosulfide solid solution cannot coexist with $β_1$ solid solution because the tie-lines between the high-form pentlandite solid solution and γ are more stable. Except for the most Fe-rich portion, the phase $β_1$ solid solution cannot yet coexist with γ because of the intervening liquid phase.

Four univariant assemblages are found in the metal-rich portion of the system as follows: (1) monosulfide solid solution ($Fe_{0.98}Ni_{0.01}S_{1.00}$) + α ($Fe_{0.96}Ni_{0.04}$) + γ ($Fe_{0.90}Ni_{0.10}$) (Kubaschewski 1982, Swartzendruber et al. 1993); (2) high-form pentlandite ($Fe_{5.07}Ni_{4.03}S_{7.90}$) + monosulfide solid solution ($Fe_{0.93}Ni_{0.05}S_{1.00}$) + γ ($Fe_{0.40}Ni_{0.60}$); (3) high-form pentlandite ($Fe_{3.03}Ni_{6.49}S_{7.48}$) + $β_1$ ($Fe_{0.71}Ni_{2.12}S_{2.00}$) + γ ($Fe_{0.25}Ni_{0.75}$); (4) $β_1$ ($Fe_{0.67}Ni_{2.32}S_{2.00}$) + liquid ($Fe_{0.12}Ni_{0.53}S_{0.35}$) + γ ($Fe_{0.21}Ni_{0.79}$).

In the S-rich portion of the system, pyrite appears at 742 ± 1 °C (Kullerud & Yoder 1959, Barton & Skinner 1979, Kubaschewski 1982) on the Fe–S join and forms a limited solid solution from FeS_2 to $Fe_{0.89}Ni_{0.11}S_{2.00}$ at 700 °C. Vaesite also has a limited solid solution from NiS_2 to $Fe_{0.29}Ni_{0.71}S_{2.00}$. Both disulfides coexist separately with S (liquid) or monosulfide solid solution. The Ni-rich end of the pyrite and Fe-rich end of the vaesite solid solution coexist and form two univariant assemblages with

monosulfide solid solution ($Fe_{0.74}Ni_{0.09}S_{1.00}$) or S (liquid).

Karup-Møller & Makovicky (1995) showed an isothermal phase diagram °C in the Fe–Ni–S system at 725 °C. Their phase relations are similar to those at 700 °C in this study. However, because phase $β_1$ and $β_2$ were not differentiated by them, the phase relations differ from those of the present study.

Phase relations at 650 °C

The isothermal phase diagram at 650 °C is shown in Figure 6. The high-form pentlandite solid solution field is slightly longer and wider (Sugaki & Kitakaze 1996, Kitakaze et al. 2011). The monosulfide solid solution still exists and retains the complete solid solution. The field for phase $β_1$ contracts to become smaller than at 700 °C. The liquid field reduces its area remarkably with decreasing temperature, but still retains a very small field slightly jutting out from the Ni–S join. The metal-rich side of the high-form pentlandite solid solution, except the Ni-rich portion, coexists with γ as at 700 °C. Phase $β_1$, except for its Ni-rich portion, can coexist with γ due to the retreat of the liquid field.

In the metal-rich portion, four univariant assemblages are found as follows: (1) monosulfide solid solution ($Fe_{0.98}Ni_{0.01}S_{1.00}$) + α ($Fe_{0.95}Ni_{0.05}$) + γ ($Fe_{0.86}Ni_{0.14}$) (Kubaschewski 1982, Swartzendruber et al. 1993); (2) high-form pentlandite ($Fe_{5.41}Ni_{3.65}S_{7.94}$) + monosulfide solid solution ($Fe_{0.89}Ni_{0.07}S_{1.00}$) + γ ($Fe_{0.36}Ni_{0.64}$); (3) high-form pentlandite ($Fe_{2.89}Ni_{6.75}S_{7.36}$) + $β_1$ ($Fe_{0.56}Ni_{2.33}S_{2.00}$) + γ
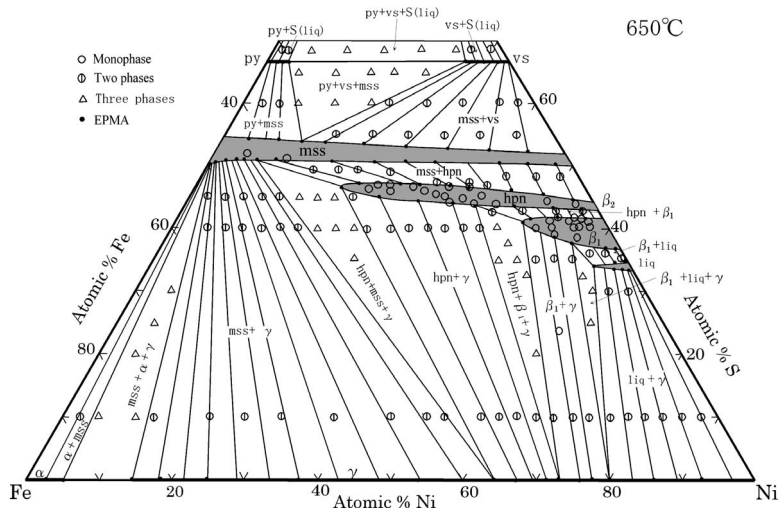
F$_{IG}$. 6. The isotherm in the Fe–Ni–S system at 650 °C in the presence of an equilibrium vapor. Abbreviations: See Table 1.

($Fe_{0.25}Ni_{0.75}$); and (4) β_1 ($Fe_{0.32}Ni_{2.95}S_{2.00}$) + liquid ($Fe_{0.02}Ni_{0.63}S_{0.35}$) + γ ($Fe_{0.23}Ni_{0.77}$).

Also, in the S-rich portion of the system, two univariant assemblages of pyrite ($Fe_{0.91}Ni_{0.09}S_{2.00}$) + vaesite ($Fe_{0.19}Ni_{0.81}S_{2.00}$) + monosulfide solid solution ($Fe_{0.65}Ni_{0.20}S_{1.00}$) or S(liquid) exist, similar to at 700 °C.

PHASE RELATION OF THE FE$_{4.5}$NI$_{4.5}$–S AND FE$_{0.9}$S–NI$_3$S$_2$ JOINS IN THE FE–NI–S SYSTEM

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

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

The low-form pentlandite with $Fe_{4.5}Ni_{4.5}S_{7.95}$ inverts to high-form at 615 °C on this join. The relations between low-form and high-form were described in detail in our previous paper (Kitakaze et al. 2011). The high-form solid solution with coexisting monosulfide solid solution is stable up to about 860 °C. However, high-form pentlandite on the metal-rich side is stable up to 750 °C, and has a solid-solution range from 45.2 to 47.0 at.% S. Above this temperature, the

solid-solution range shrinks with increasing temperature, and the metal-rich composition varies. Finely, high-form pentlandite ($Fe_{4.93}Ni_{4.06}S_{8.01}$) melts as a pseudoperitectic reaction at 865 °C, changing to a mixture of monosulfide solid-solution and liquid as seen in the Figure.

Phase relations along the Fe$_{0.9}$S–Ni$_3$S$_2$ join

We considered a pseudo-binary phase diagram for the $Fe_{0.9}S$–Ni_3S_2 join, passing through the ideal composition of pentlandite in the system at temperatures from 600 to 950 °C, as shown Figure 8. On the this join, the phase relations below 650 °C are complicated and are described in a previous paper (Kitakaze et al. 2011).

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

DISCUSSION

Pentlandite stability

No phase corresponding to high-form pentlandite solid solution including $Fe_{4.5}Ni_{4.5}S_{8.0}$ was found at temperatures above 610 °C by Kullerud (1963a, b), Kullerud et al. (1969), or Hsieh et al. (1982). However, Sugaki et al. (1983, 1984) found an extensive field for high-form pentlandite with more Fe-rich compositions than $Fe_{4.5}Ni_{4.5}S_{8.0}$ to $Ni_{3\pm x}S_2$
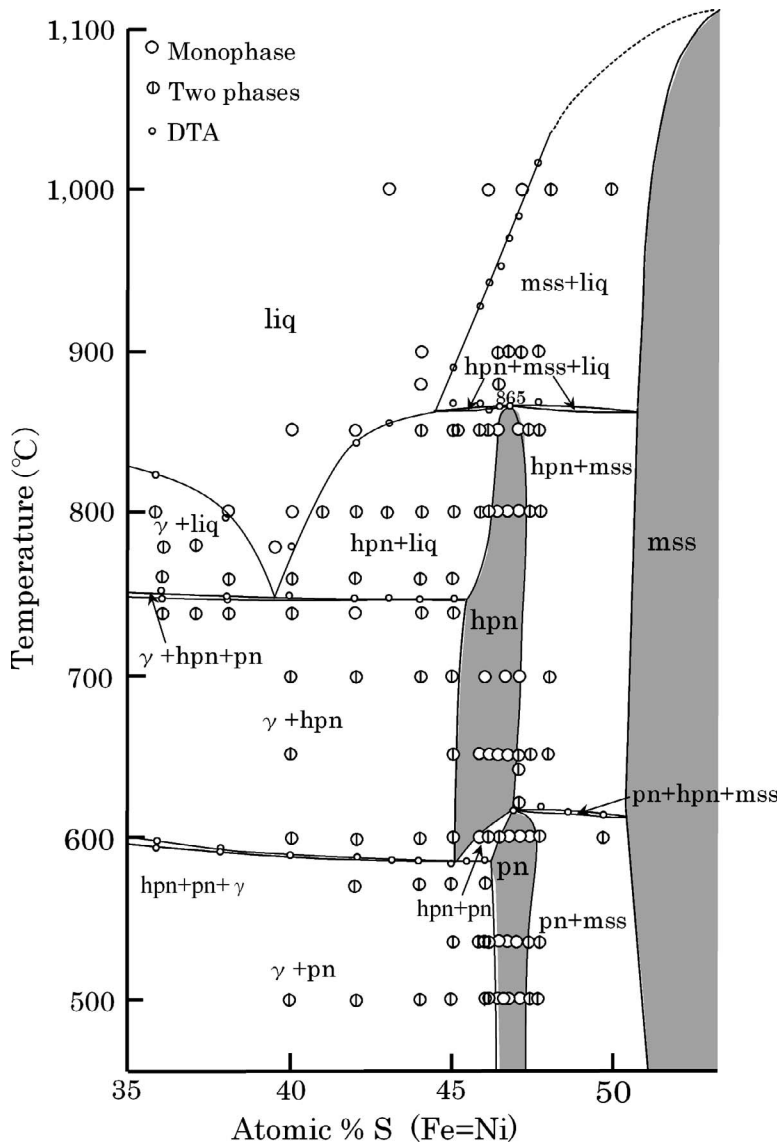
FIG. 7. The phase diagram of the sulfur composition *versus* the temperature with Fe=Ni in the Fe–Ni–S system with additional data from Sugaki & Kitakaze (1998) and Kitakaze *et al.* (2011). All phases and phase assemblages coexist with vapor. Abbreviations: See Table 1; liq = liquid.

along the Ni–S boundary at 800 and 650 °C. Hayashi *et al.* (1985) and Hayashi (1985) also recognized the existence of this same solid solution in equilibrium experiments for the quaternary Cu–Fe–Ni–S system at 850 °C, and 800, 650, and 600 °C, respectively. Fedorova & Sinyakova (1993) investigated the isothermal phase relations in the Fe–Ni–S system at 900, 820, and 600 °C, and reported an extended heazlewoodite solid solution $(Fe_xNi_{1-x})_{3\pm y}S_2$ at 820 and 600

°C, with limited pentlandite solid solution. Karup-Møller & Makovicky (1995) showed an elongated field for $(Fe,Ni)_{3\pm x}S_2$ in the phase diagram at 725 °C. Both solid solutions correspond to the high-form pentlandite–$Ni_{3\pm x}S_2$ solid-solution of Sugaki *et al.* (1983, 1984) and Kitakaze *et al.* (2011).

A Ni-rich ternary phase $(Ni,Fe)_{3\pm x}S_2$ in the Ni-rich portion of the system was documented at 862 °C by Kullerud (1963b) and Kullerud *et al.* (1969). A ternary
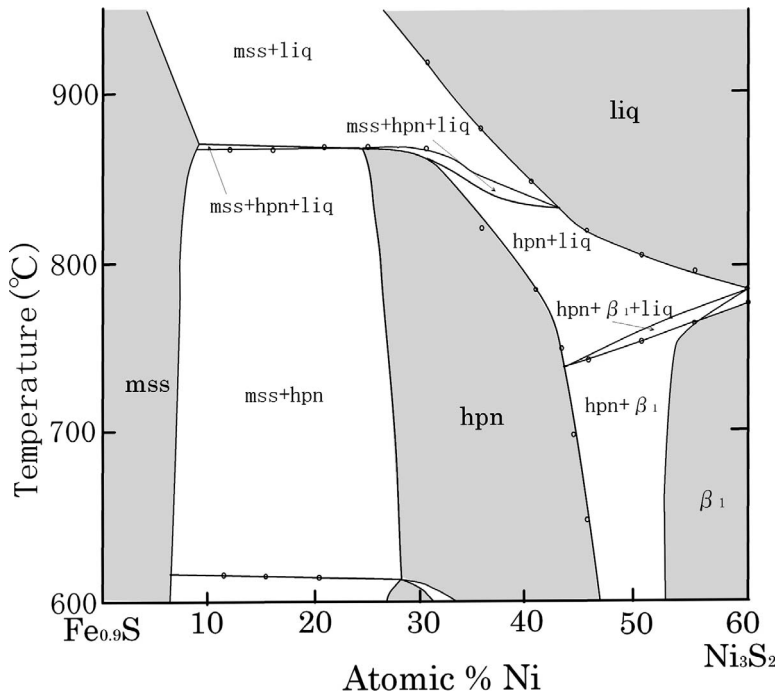
F_IG. 8. The phase diagram of the pseudobinary from 0 to 60 at.% Ni in the $Fe_{0.9}S$–Ni_3S_2 join in the Fe–Ni–S system. All phases and phase assemblages coexist with vapor. Abbreviation: See Table 1; liq = liquid.

phase β with a limited solid-solution at 850 °C was also described by Hsieh *et al.* (1982). However, these phases are located in the liquid field or along its S-rich boundary at 850 °C in this study, except for a small S-rich part of phase β.

High-form pentlandite with composition $Fe_{4.94}Ni_{4.06}$ $S_{8.00}$ appears earliest at 870 ± 3 °C *via* a pseudoperitectic reaction between monosulfide solid solution and liquid in the system. This precipitation by the pseudoperitectic reaction terminates when the high-form solid solution extends its composition to reach the Ni–S join to include phase $β_2$ at 806 ± 3 °C. It is noticeable that the appearance of the high-form is so fast as to form the extensive solid solution on cooling in only 64 °C from 870 to 806 °C. After the pseudo-peritectic reaction, the crystallization of the high-form from the liquid by pseudoeutectic reaction continues with decreasing temperature down to 739 ± 3 °C, at which point the tie-line of the liquid–high-form pentlandite changes into those of the $β_1$–γ phases. Fedorova & Sinyakova (1993) also stated that the heazlewoodite solid solution (high-form pentlandite solid solution) forms by a peritectic reaction between monosulfide solid solution and liquid below 876 °C. Karup-Møller & Makovicky (1995) suggested that liquid (sulfide melt)–monosulfide solid-solution frac-

tionation is replaced by liquid–$(Fe,Ni)_{3\pm x}S_2$ fraction-ation just below 850 °C, and this fractionation persists down to 635 °C, at which temperature the liquid in the Ni–S join solidifies (Kullerud & Yund 1962). According to our study, the tie-line between liquid and high-form pentlandite persists at temperatures from 870 ± 3 °C to 739 ± 3 °C, but no such tie-lines exist below 739 ± 3 °C. Similarly, liquid–monosulfide solid solution tie-lines persist down to 762 ± 3 °C, but no such tie-lines are found below this temperature.

Pentlandite ore genesis

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

Fe–Ni–S) (Sugaki *et al.* 1983, 1984, Fedorova & Sinyakova 1993, Karup-Møller & Makovicky 1995, Sugaki & Kitakaze 1998, Kitakaze *et al.* 2011); (2) exsolution from the S-rich 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 (Kitakaze *et al.* 2011); and (3) an exsolution of the metal-rich boundary of the monosulfide solid solution below 625 °C for the S-rich extremity of the pentlandite solid solution as a narrow rim on a S-richer portion (Edwards 1954, Hawley 1962, Naldrett *et al.* 1967, Francis *et al.* 1976, Ramdohr 1980, Craig & Vaughan 1981, Fedorova & Sinyakova 1993, Kitakaze *et al.* 2011).

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