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Chapter 1.3.2

# HYDROTHERMAL SYNTHESIS OF PENTLANDITE

Asahiko SUGAKI[1] and Arashi KITAKAZE[2]

[1]*4-30-503 Kadan, Sendai 980, Japan*
[2]*Institute of Mineralogy, Petrology and Economic Geology, Faculty of Science, Tohoku University, Sendai 980, Japan*

## 1. *Introduction*

Hydrothermal synthesis of pentlandite ($Fe_{4.5}Ni_{4.5}S_8$) was difficult as reported by SHIMA *et al.* (1987). The present authors also tried to hydrothermally synthesize pentlandite in the course of equilibrium studies of the Fe–Ni–S system at low temperature. However, the first synthesis attempt using a common recrystallization method (SCOTT and BARNES, 1971; SUGAKI *et al.*, 1975) failed because hydrothermal conditions had higher oxygen and sulfur fugacities ($f_{O_2}$, $f_{S_2}$) than those of pentlandite. Thus, a trial decreasing both the $f_{O_2}$ and $f_{S_2}$ of the hydrothermal solution was done as mentioned below, and pentlandite consequently was synthesized.

In this paper, the hydrothermal synthesis of pentlandite and its mineralogical data are described.

## 2. *Hydrothermal Synthesis*

The hydrothermal synthesis of pentlandite was first attempted by ways similar to those of SCOTT and BARNES (1971) and SUGAKI *et al.* (1975), using synthetic (dry method) pentlandite as a starting material, $NH_4Cl$ (5 m) as a solvent and transport solution, and a gold tube as a container. However, pentlandite was not synthesized, and a mixture of mono-sulfide solid solution (mss) and magnetite, instead of pentlandite, was precipitated. To prevent the formation of magnetite and mss and to obtain favorable conditions for pentlandite crystallization, both the $f_{O_2}$ and $f_{S_2}$ of the solvent aqueous solution were buffered by hydrogen generated by the reaction between powdered electrolytic iron (99.999%) and distilled water in a platinum tube. The platinum tube (2 mm in outside diameter, 0.15 mm thick, 40 mm long) was inserted into a silica glass tube (4 mm in inside diameter, 80 mm long) of a reaction vessel, as shown in Fig. 1. Mss, pentlandite and a

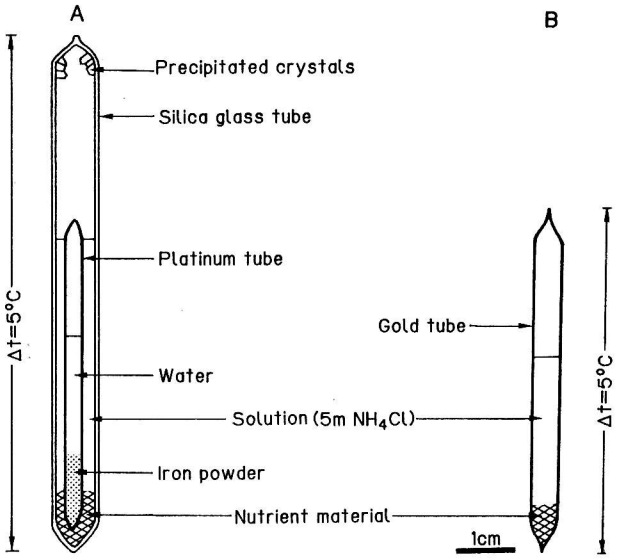


FIG. 1. Schematic sketch of reaction vessels for hydrothermal synthesis of pentlandite (A) in comparison with normal recrystallization method (B).

mixture of them synthesized by the dry method were used as starting material. As a solvent and transport agent, 5 m $NH_4Cl$ aqueous solution was also employed. The thermal gradient of the reaction vessel was 0.6° to 0.7°C/cm and the temperature difference between the hot (bottom of the tube) and cool (top of the tube) ends was 5°C at 400°C. The silica glass tube was put into a test-tube type pressure vessel with an electric furnace. The synthetic experiments were carried out at 300°, 350° and 400°C for 7, 14 and 20 days, and synthetic products precipitated as a fine crystal aggregate on the inside wall of the silica tube at the cool (top) end. The experimental results are given in Table 1. Pentlandite crystallized at temperatures from 300° to 400°C as a monophase or assemblage with mss or heazlewoodite (Fig. 2).

### 3. *Mineralogical Data for Synthetic Pentlandite*

Pentlandite precipitated hydrothermally is a fine-grained octahedral crystal, 5 to 40 $\mu$m in size, often associated with mss of hexagonal platy crystals (Fig. 2). Reflectivities of synthetic pentlandite, measured by a Leitz MPV-II microscopic photometer, are 31.5% (406 nm), 36.7% (436 nm), 41.8% (480 nm), 48.3% (546 nm), 50.5% (586 nm) and 52.2% (648 nm). X-ray powder diffraction data for synthetic pentlandite are given in Table 2 in comparison with that of pentlandite from Sudbury. Both the data are in

TABLE 1. Experimental results for hydrothermal synthesis of pentlandite.

| Run No. | Bulk composition (wt%) | | | Mineral assemblage | Temp. (°C) | Press. (kgf/cm$^2$) | Time (days) | Products |
|---|---|---|---|---|---|---|---|---|
| | Fe | Ni | S | | | | | |
| HFNS 012 | 38.57 | 15.00 | 46.43 | pn+mss | 400 | 300 | 7 | pn+mss |
| HFNS 013 | 33.57 | 20.00 | 46.43 | pn+mss | 400 | 300 | 7 | pn |
| HFNS 014 | 28.57 | 25.00 | 46.43 | pn+mss | 400 | 300 | 7 | pn+mss |
| HFNS 027 | 23.57 | 30.00 | 46.43 | pn | 400 | 300 | 14 | pn |
| HFNS 028 | 18.57 | 35.00 | 46.43 | pn | 400 | 300 | 14 | pn |
| HFNS 029 | 13.57 | 40.00 | 46.43 | hz+mss | 400 | 300 | 14 | pn+hz |
| HFNS 019 | 33.57 | 20.00 | 46.43 | pn+mss | 350 | 300 | 20 | mss |
| HFNS 020 | 28.57 | 25.00 | 46.43 | pn+mss | 350 | 300 | 20 | mss |
| HFNS 021 | 23.57 | 30.00 | 46.43 | pn | 350 | 300 | 20 | mss+pn |
| HFNS 022 | 18.57 | 35.00 | 46.43 | pn | 350 | 300 | 20 | mss+pn |
| HFNS 024 | 33.57 | 20.00 | 46.43 | pn+mss | 300 | 300 | 20 | mss+pn |
| HFNS 025 | 28.57 | 25.00 | 46.43 | pn+mss | 300 | 300 | 20 | mss+pn |
| HFNS 026 | 23.57 | 30.00 | 46.43 | pn | 300 | 300 | 20 | mss+pn |

pn: pentlandite, mss: monosulfide solid solution, hz: heazlewoodite.

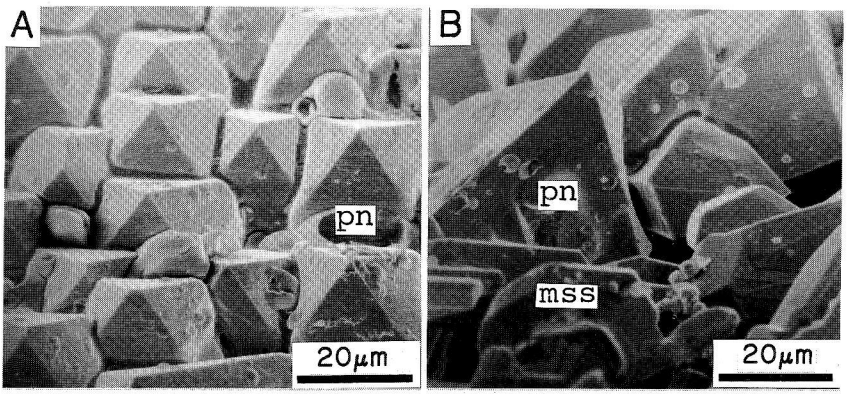


FIG. 2. Scanning electron images of pentlandite (pn) and monosulfide solid solution (mss) synthesized hydrothermally at 400°C. A: Octahedral crystals of pentlandite, B: Assemblage of pentlandite and mss.

good accordance with each other. The cell constant ($a$=10.115 Å) for the synthetic one is slightly larger than that of the Sudbury pentlandite. Analytical data obtained by EPMA for pentlandite synthesized at 400°C are also given in Table 3 together with those of mss and heazlewoodite. Pentlandite at 400°C has a limited solid solution, as shown in Fig. 3.

TABLE 2. X-ray powder data of pentlandite synthesized hydrothermally at 400°C.

| *hkl* | Synthetic* | | | Sudbury** | |
|---|---|---|---|---|---|
| | *I* | *d* (obs) | *d* (calc) | *I* | *d* |
| 111 | 24 | 5.84 | 5.84 | 30 | 5.78 |
| 002 | 5 | 5.05 | 5.06 | 5 | 5.01 |
| 022 | 6 | 3.58 | 3.58 | 5 | 3.55 |
| 113 | 60 | 3.05 | 3.05 | 80 | 3.03 |
| 222 | 25 | 2.919 | 2.920 | 40 | 2.90 |
| 004 | 5 | 2.530 | 2.529 | 2 | 2.51 |
| 133 | 15 | 2.320 | 2.320 | 30 | 2.30 |
| 024 | 4 | 2.261 | 2.262 | 5 | 2.25 |
| 115 | 40 | 1.946 | 1.947 | 50 | 1.931 |
| 044 | 100 | 1.788 | 1.788 | 100 | 1.775 |
| 135 | 5 | 1.710 | 1.710 | 5 | 1.697 |
| 335 | 10 | 1.543 | 1.542 | 10 | 1.530 |
| 226 | 10 | 1.525 | 1.525 | 10 | 1.514 |
| 355 | 20 | 1.317 | 1.317 | 20 | 1.307 |
| 008 | 20 | 1.264 | 1.264 | 20 | 1.255 |
| 157 | 13 | 1.168 | 1.168 | 5 | 1.160 |
| | $a$=10.115 Å | | | $a$=10.042 Å | |

*HFNS 014.
**Worthington mine, Sudbury (JCPDS 8-90).

TABLE 3. Analytical data by EPMA for pentlandite and monosulfide solid solution (mss) synthesized at 400°C.

| Phases | Weight % | | | | Atomic % | | |
|---|---|---|---|---|---|---|---|
| | Fe | Ni | S | Total | Fe | Ni | S |
| HFNS 012 | | | | | | | |
| pn | 32.8 | 33.6 | 33.1 | 99.5 | 26.7 | 26.1 | 47.2 |
| mss | 41.7 | 21.4 | 36.9 | 100.0 | 33.0 | 16.1 | 50.9 |
| HFNS 014 | | | | | | | |
| pn | 30.4 | 36.7 | 33.3 | 100.4 | 24.7 | 28.3 | 47.0 |
| mss | 34.1 | 29.5 | 36.6 | 100.2 | 27.1 | 22.3 | 50.6 |
| HFNS 027 | | | | | | | |
| pn | 29.6 | 36.7 | 33.0 | 99.3 | 24.3 | 28.7 | 47.1 |
| HFNS 029 | | | | | | | |
| pn | 30.0 | 36.6 | 32.5 | 99.1 | 24.7 | 28.7 | 46.6 |
| hz | 3.8 | 69.1 | 26.3 | 99.2 | 3.3 | 57.0 | 39.7 |

pn: pentlandite, mss: monosulfide solid solution,
hz: heazlewoodite.

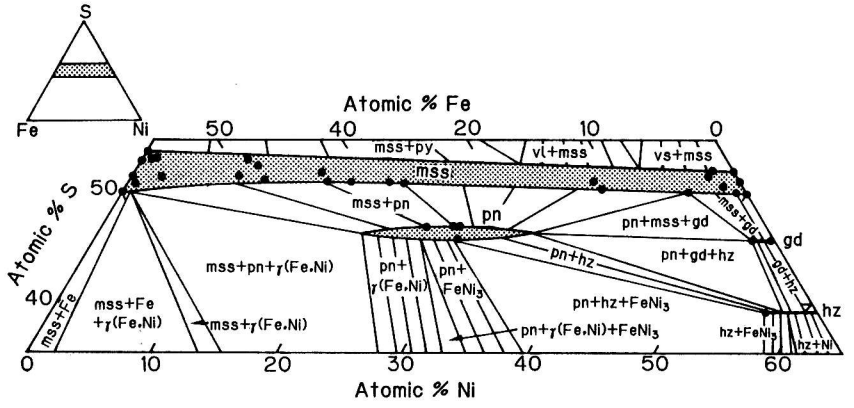


FIG. 3. Phase relations around pentlandite in the Fe–Ni–S system at 400°C. gd: godlevskite, hz: heazlewoodite, mss: monosulfide solid solution, pn: pentlandite, py: pyrite, vl: violarite, vs: vaesite.

## 4. *Phase Relations around Pentlandite in the Fe–Ni–S System*

From the experimental results, the phase relations around pentlandite at 400°C are shown in Fig. 3. Pentlandite which has a solid solution assembles with mss, godlevskite, heazlewoodite, (Fe, Ni) and $FeNi_3$. However, pentlandite cannot associate with violarite, pyrite, and vaesite because a continuous solid solution of mss exists stably. The phase relations as above nicely agree with those obtained by the dry method (SHEWMAN and CLARK, 1970; CRAIG, 1973).

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