

PHOSPHIDE SOLID-SOLUTIONS WITHIN THE METAL-RICH PORTION OF THE QUATERNARY SYSTEM Co–Fe–Ni–P AT 800°C, AND MINERALOGICAL IMPLICATIONS

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ABSTRACT

Solid solutions within the system Co–Fe–Ni–P were studied experimentally at 800°C by means of the evacuated silica tube technique. Three broad solid-solution series were detected in the system, tetragonal ϕ , (Co,Ni,Fe)₃P, hexagonal λ_1 , (Co,Ni,Fe)₂P, and orthorhombic λ_2 , (Co,Ni,Fe)₂P. All phosphides known as minerals are situated within these three pseudoternary systems. Cobalt has a remarkable influence on the structure type of (Co,Fe,Ni)₂P solid solutions, inducing a transition of the hexagonal structure (rich in Fe, Ni) to orthorhombic (rich in Co). Nevertheless, the cobalt content reported in allabogdanite is too low to bring about the transition of the hexagonal λ_1 structure to the orthorhombic λ_2 structure. In addition to these solid-solution series, two binary series were detected: a tetragonal one, (Co,Ni)₁₂P₅, and over a very narrow field of stability, (Co,Ni)₅P₂, which is hexagonal. Phosphides with such compositions can be expected in meteorites, in close association with other phosphides.

Keywords: phase relations, phosphides, schreibersite, nickelporphide, barringerite, allabogdanite, Co, Fe, Ni, meteorites.

SOMMAIRE

Les solutions solides du système Co–Fe–Ni–P ont fait l'objet d'études expérimentales à 800°C par la méthode des tubes en silice scellés et évacués. Trois grandes séries de solutions solides sont connues dans ce système, la phase tétragonale ϕ , (Co,Ni,Fe)₃P, la phase hexagonale λ_1 , (Co,Ni,Fe)₂P, et la phase orthorhombique λ_2 , (Co,Ni,Fe)₂P. Tous les phosphures connus comme minéraux ont une composition dans un de ces trois systèmes pseudoternaires. Le cobalt exerce une influence remarquable sur la structure des solutions solides (Co,Fe,Ni)₂P, menant à une transition de la structure hexagonale (compositions riches en Fe, Ni) à celle de symétrie orthorhombique (compositions riches en Co). Toutefois, le contenu de l'allabogdanite en cobalt est trop faible pour induire une transition de la structure hexagonale λ_1 à la structure orthorhombique λ_2 . En plus de ces séries de solutions solides, il y a deux séries binaires: structure tétragonale (Co,Ni)₁₂P₅, et un champ de stabilité très étroit de (Co,Ni)₅P₂, phase hexagonale. On peut s'attendre à trouver des phosphures de telles compositions dans les météorites, en association avec d'autres phosphures.

(Traduit par la Rédaction)

Mots-clés: relations de phases, phosphures, schreibersite, nickelporphide, barringerite, allabogdanite, Co, Fe, Ni, météorites.

INTRODUCTION

Four minerals are known whose composition falls inside the quaternary system Co–Fe–Ni–P: schreibersite [(Fe,Ni)₃P], nickelporphide [(Ni,Fe)₃P], barringerite [(Fe,Ni)₂P] and allabogdanite (Fe_{1.5}Ni_{0.5})P. In order to establish the solubility limits of Co in such Fe–Ni phosphides and the influence of Co on the properties of these minerals, solid solutions within the metal-rich portion of the quaternary system Co–Fe–Ni–P were investigated at 800°C. The variation of unit-cell dimensions with the chemical composition of the solid

solution with a 3:1 metal:P ratio was studied in detail, whereas solid solutions with the 2:1 metal:P ratio were studied in a cursory way.

BACKGROUND INFORMATION

Crystal-structure data of phosphides described as minerals are summarized in Table 1. Schreibersite, an iron–nickel phosphide with a 3:1 ratio, is a common accessory mineral in differentiated meteorites represented by meteoritic irons and stony irons. During the cooling of the parent bodies of iron meteorites,

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schreibersite apparently nucleates within the subsolidus temperature range of 800–400°C (Clarke & Goldstein 1978, Geist *et al.* 2004). It occurs closely associated with kamacite, cohenite, troilite, and sphalerite (*e.g.*, Keil & Anderson 1965, Clarke & Goldstein 1978, El Goresy *et al.* 1988, Kimura 1988, Ikeda 1989) and silicates (Benedix *et al.* 1998). Clarke & Goldstein (1978) distinguished four major types of schreibersite in iron meteorites and discussed the role that schreibersite growth played in coarse-grained iron meteorites.

Nickelphosphide was first described in association with kamacite and taenite from the ungrouped plesitic Butler octahedrite (Britvin *et al.* 1999). Kopylova *et al.* (1999) described nickelphosphide from the Onello ataxite, and Skála & Frýda (1999) independently described nickelphosphide from the Vicenice octahedrite.

The 2:1 Fe–Ni phosphide is a rare accessory mineral. Barringerite was first described from the Ollague pallasite by Buseck (1969), and Brandstätter *et al.* (1991) found barringerite in a lunar meteorite. There is an uncertainty as to whether barringerite may have formed terrestrially in the Ollague pallasite (Doan 1969, Buchwald 1975). Nevertheless, terrestrial weathering and artificial heating in the case of the lunar meteorite Y-793274 can be ruled out (Brandstätter *et al.* 1991). Recently, Yang *et al.* (2005) reported barringerite in a terrestrial garnet peridotite from China.

Allabogdanite was described by Britvin *et al.* (2002) from the Onello meteorite, in close association with nickelphosphide, schreibersite, awaruite and graphite. According to Britvin *et al.* (2002), allabogdanite is very likely a primary phase in the Onello meteorite, and it probably crystallized at the first stages of crystallization of the Fe–Ni melt. Schreibersite in the Onello meteorite is a secondary mineral (Britvin *et al.* 2002).

Chemical analyses of Fe–Ni phosphides (*e.g.*, Papike 1998) show that next to metallic phases, phosphides are the most important collectors of Co in meteorites, in the

form of compounds like (Fe,Ni,Co)₃P or (Fe,Ni,Co)₂P. Nevertheless, the Co contents in natural phosphides are generally quite low, in line with the low concentrations of Co in meteorites. Bulk contents of Co in stony and iron meteorites vary over the range 0.02–0.136 wt% and ~0.4–0.6 wt%, respectively (Wiik 1969). Cobalt contents reported in schreibersite range from ~0.14 to 0.39 wt% (Keil 1968, Leitch & Smith 1982, El Goresy *et al.* 1988, Ikeda 1989). The schreibersite from the Blithfield meteorite, which contains 29.3 wt% Co (Rubin 1984), is exceptional.

The Co content in barringerite from the Ollague pallasite (Buseck 1969) is negligible, and allabogdanite reported from the Onello iron meteorite contains 1.4 wt% Co (Britvin *et al.* 2002).

Furthermore, Co contents have a substantial influence on the crystal structure of phosphides with a 2:1 metal:P ratio, by inducing a transition of the hexagonal structure to an orthorhombic modification (Fruchart *et al.* 1969).

PREVIOUS EXPERIMENTAL FINDINGS

The binary systems Co–P, Fe–P and Ni–P

The results of experiments have been critically evaluated by Massalski (1992). Seven binary phases were found to be stable within these systems. Their composition and the crystal-structure data are summarized in Table 2. Lee & Nash (1991) reported Fe₃P and Fe₂P as the stable phases in the metal-rich portion of the system Fe–P. From the system Ni–P, Okamoto (1991) reported four stable phases: Ni₃P, Ni₂P, Ni₂P₅ and Ni₁₂P₅; from the system Co–P, Ishida & Nishizawa (1991) reported one binary phase Co₂P.

TABLE 2. CRYSTAL-STRUCTURE DATA OF BINARY PHASES IN THE SYSTEM Co-Fe-Ni-P

Phase	Symmetry	Space group	Cell parameters	Reference
Fe ₃ P	Tetragonal	<i>I</i> $\bar{4}$	<i>a</i> 9.1081(3) <i>c</i> 4.4606(2)	Liu <i>et al.</i> (1998)
Fe ₂ P	Hexagonal	<i>P</i> $\bar{6}2m$	<i>a</i> 5.859(2) <i>c</i> 3.382(1)	Larsson (1964)
Ni ₃ P	Tetragonal	<i>I</i> $\bar{4}$	<i>a</i> 8.954 <i>c</i> 4.386	Rundqvist <i>et al.</i> (1962)
Ni ₂ P	Hexagonal	<i>P</i> $\bar{6}2m$	<i>a</i> 5.859 <i>c</i> 3.385	Rundqvist & Jellinek (1959)
Ni ₂ P ₅	Hexagonal	<i>P</i> $\bar{3}c$	<i>a</i> 13.220(2) <i>c</i> 24.632(2)	Saini <i>et al.</i> (1964)
Ni ₁₂ P ₅	Tetragonal	<i>I</i> 4/ <i>m</i>	<i>a</i> 8.646 <i>c</i> 5.070	Larsson (1964)
Co ₂ P	Orthorhombic	<i>Pnma</i>	<i>a</i> 5.6490(3) <i>b</i> 3.5126(2) <i>c</i> 6.6071(3)	Skála & Drábek (2001)
β-Co ₂ P*	Hexagonal	<i>P</i> $\bar{6}2m$	<i>a</i> 5.742(2) <i>c</i> 3.457(5)	Ellner & Mittemeijer (2001)

* stable above 1659 K (Ellner & Mittemeijer 2001). Cell parameters are in Å.

TABLE 1. CRYSTAL-STRUCTURE DATA FOR MINERALS IN THE SYSTEM Co-Fe-Ni-P

Phase	Symmetry	Space group	Cell parameters Å	Reference
Schreibersite (Fe,Ni) ₃ P	Tetragonal	<i>I</i> $\bar{4}$	<i>a</i> 9.0400 <i>c</i> 4.4620	Doenitz (1970)
Nickelphosphide (Ni,Fe) ₂ P	Tetragonal	<i>I</i> $\bar{4}$	<i>a</i> 5.748(2) <i>b</i> 3.548(1) <i>c</i> 6.661(2)	Britvin <i>et al.</i> (1999)
Barringerite (Fe,Ni) ₂ P	Hexagonal	<i>P</i> $\bar{6}2m$	<i>a</i> 5.87 <i>c</i> 3.43	Buseck (1969)
Allabogdanite (Fe,Ni) ₂ P	Orthorhombic	<i>Pnma</i>	<i>a</i> 5.792(7) <i>b</i> 3.564(4) <i>c</i> 6.691(8)	Britvin <i>et al.</i> (2002)

Fe-Ni-P

Vogel & Baur (1931) examined the metal-rich section of the system from the metallurgical point of view. They found a complete solid-solution ($\text{Fe}_{1-x}\text{Ni}_x$)₃P and quoted Fe₃P, Fe₂P, Ni₅P₂ and Ni₃P as stable phases in the system. Doan & Goldstein (1970) studied the nickel-rich portion of the system (up to 16.6 wt% P) in the temperature range 1100–550°C. They reported a complete tetragonal ($\text{Fe}_{1-x}\text{Ni}_x$)₃P solid solution in the temperature range 995 to 550°C. These authors studied in detail the phase relations of ($\text{Fe}_{1-x}\text{Ni}_x$)₃P solid solution and Fe–Ni alloys. A complete hexagonal solid-solution ($\text{Fe}_{1-x}\text{Ni}_x$)₂P was synthesized at 850 and 900°C by Fruchart *et al.* (1969).

Fe-Co-P

Phase relations within the system Fe–Co–P were first described by Berak (1951) and later summarized by Villars *et al.* (1995). Three phases are stable in the metal-rich part of the system: Co₂P, Fe₂P, and Fe₃P. Furthermore, they reported three solid solutions: ($\text{Fe}_{1-x}\text{Co}_x$)₃P, hexagonal ($\text{Fe}_{1-x}\text{Co}_x$)₂P and orthorhombic ($\text{Fe}_{1-x}\text{Co}_x$)₂P. There is no compound with the composition Co₃P corresponding to Fe₃P (Villars *et al.* 1995, Ishida & Nishizawa 1991).

The literature data concerning the maximum solubility of cobalt in Fe₃P are not uniform. The maximum solubility of cobalt in Fe₃P at 900°C is 45 at.% and rapidly decreases with temperature, falling to about 10 at.% below 700°C (Berak 1951). According to Liu *et al.* (1998), the ($\text{Fe}_{1-x}\text{Co}_x$)₃P solid solution is restricted to $x < 0.37$ (27.7 at.% Co), and the replacement of iron by cobalt decreases the unit-cell parameters of the ($\text{Fe}_{1-x}\text{Co}_x$)₃P phase.

Between Fe₂P and Co₂P, two broad solid-solutions have been described (Berak 1951, Vos *et al.* 1962, Fruchart *et al.* 1969, Roger *et al.* 1969, Maeda & Takashima, 1973). Depending on their Fe and Co contents, ($\text{Co}_{1-x}\text{Fe}_x$)₂P phosphides crystallize in a hexagonal or an orthorhombic structure, designated as λ_1 and λ_2 , respectively, by Villars *et al.* (1955). For x from 0.84 to 1, the solid solution is hexagonal, whereas for x between 0 and 0.84, it is orthorhombic (Fruchart *et al.* 1969). According to the same authors, the two-phase region $\lambda_1 + \lambda_2$ is very narrow, spanning 0.7 at.% Co at 600°C and 2.7 at.% Co at 950°C.

Co-Ni-P

No phase diagram of the Co–Ni–P system is available in the literature.

Fruchart *et al.* (1969) and Roger *et al.* (1969) reported hexagonal and orthorhombic ($\text{Co}_{1-x}\text{Ni}_x$)₂P solid solutions. The field of the nickel-rich hexagonal solid solution is very broad, whereas that of the cobalt-

rich orthorhombic solid-solution is restricted only to $x \leq 0.15$.

Co-Fe-Ni-P

Phase relations in the quaternary system Co–Fe–Ni–P have never been studied. Drábek & Skála (2002) published a preliminary report concerning phase relations within the pseudoternary system Co₂P–Fe₂P–Ni₂P at 800°C and reported two broad solid-solution series of hexagonal and orthorhombic (Co,Fe,Ni)₂P. Drábek (2004) presented the first results concerning solid solutions within the metal-rich section of the system Co–Fe–Ni–P and described the existence of three quaternary and two ternary solid-solutions.

EXPERIMENTAL

Experiments were performed in evacuated and sealed silica-glass tubes in horizontal tube furnaces. Temperatures were measured with PtRh10–Pt thermocouples and are accurate to $\pm 3^\circ\text{C}$. The digital thermometer was periodically calibrated against the melting point of ice. To shorten reaction times, the charges were repeatedly ground (1–3 times) under acetone and reheated to 800°C. The 800°C isothermal section was selected because of satisfactory reaction-kinetics at this temperature. This temperature represents also the upper limit of nucleation of schreibersite during cooling of the parent bodies (Geist *et al.* 2004). After each run, the silica-glass tubes were quenched in ice water. Phosphides were synthesized from cobalt powder (Koch-Light Laboratory, 99.5% purity), iron powder, 99.998% (PURATRONIC, Alfa, A Johnson Matthey Company), nickel powder 99.999% (SPEX Ind. Inc.) and red phosphorus lump, 99.999% (Aldrich Chem. Co.). Before reactions, the metals were reduced in a stream of hydrogen for four hours at 800°C.

Run products were examined by optical microscopy, with an electron microprobe, and by X-ray powder diffraction. The homogeneity of solid solutions could be reliably checked by reflected-light microscopy. However, most polyphase run-products are fine-grained intimate intergrowths whose differentiation was hampered by the fact that the optical properties of product phosphides are very similar. X-ray diffraction was the most reliable technique to determine phase composition of the run products, particularly to distinguish between hexagonal and orthorhombic (Co,Fe,Ni)₂P solid solutions. The first appearance of the 210 reflection of hexagonal (Co,Fe,Ni)₂P and of the 211 reflection of orthorhombic (Co,Fe,Ni)₂P was used as the indicator of the presence of these phases. These reflections can be recorded where the phases were present in quantities exceeding ~ 2 at.%.

The Philips X'Pert MPD system with a vertical goniometer in the Bragg–Brentano reflecting geometry,

cobalt radiation, a secondary beam graphite monochromator and a proportional counter were used to collect X-ray powder data. Samples were placed on a low-background silicon holder. Step-scanned data were collected in the angular range 20–145° 2 θ with a step size 0.02° and 8 seconds of exposure per step.

The whole profile-fitting method (WPPF) was applied to calculate unit-cell parameters from powder data. The program used for calculations is FULLPROF (Rodríguez-Carvajal 2001).

EXPERIMENTAL RESULTS

Experiments revealed the existence of three broad quaternary solid-solutions, (a) tetragonal (Co,Ni,Fe)₃P, (b) hexagonal λ_1 (Co,Ni,Fe)₂P, and (c) orthorhombic λ_2 (Co,Ni,Fe)₂P. In addition, ternary tetragonal (Co,Ni)₁₂P₅ and hexagonal (NiCo)₅P₂ solid solutions were documented. The position of the solid solutions studied within the Co – Fe – Ni – P tetrahedron is shown schematically in Figure 1.

The pseudoternary system

“Co₃P” – Fe₃P – Ni₃P at 800°C

The 800°C isothermal section of the pseudoternary system Co₃P – Fe₃P – Ni₃P is shown in Figure 2, and the results of representative experiments are presented in Table 3. The tetragonal ϕ (Fe,Ni,Co)₃P solid-solution dominates the system, forming a wide field that includes

the whole Fe₃P–Ni₃P side. The solubility of “Co₃P” in the ϕ (Fe,Ni,Co)₃P solid solution slightly increases linearly with increasing Ni content. Along the “Co₃P” – Fe₃P side, the solid solution reaches up to 41 mol.% Co₃P (31 at.%), and along the “Co₃P”–Ni₃P side, it extends up to 52 mol.% Co₃P (39 at.%). In the ϕ solid solution with a 1:1 Fe : Ni ratio, the solubility of “Co₃P” extends to 46 mol.% Co₃P. The “Co₃P” corner of the system is occupied by a quaternary five-phase field.

The unit-cell dimensions vary with the chemical composition of the ϕ (Co,Fe,Ni)₃P solid solution. The variation of unit-cell dimensions of (Fe,Ni)₃P solid solution with composition has been reported by Skála & Drábek (2000) and, therefore, the current research

TABLE 3. EXPERIMENTS IN THE PSEUDOTERNARY SYSTEM Co₃P–Fe₃P–Ni₃P PERFORMED AT 800°C

Expt. no.	Starting mixture mol.%			Time hours	Products
	Co ₃ P	Fe ₃ P	Ni ₃ P		
P80	40.00	60.00	–	323	ϕ
P196	50.00	25.00	25.00	300	$\phi + >\lambda_1$
P208	45.95	27.03	27.03	669	ϕ
P262	50.00	14.29	35.71	257	$\phi + >\lambda_1 + >>Co$
P277	41.67	58.33	–	1380	$\phi + >\lambda_1$
P280	50.00	–	50.00	1280	ϕ
P285	44.12	44.12	11.76	232	$\phi + >\lambda_2$
P286	53.33	6.67	40.00	162	$\phi + >\lambda_1 + >>Co$
P315	53.15	–	46.88	160	$\phi + \lambda_1 + Co + Ni_{12}P_5?$
P317	36.11	55.56	8.33	1008	ϕ
P326	48.15	14.89	37.04	51	$\phi + >\lambda_1$
P339	45.45	36.36	18.18	432	ϕ

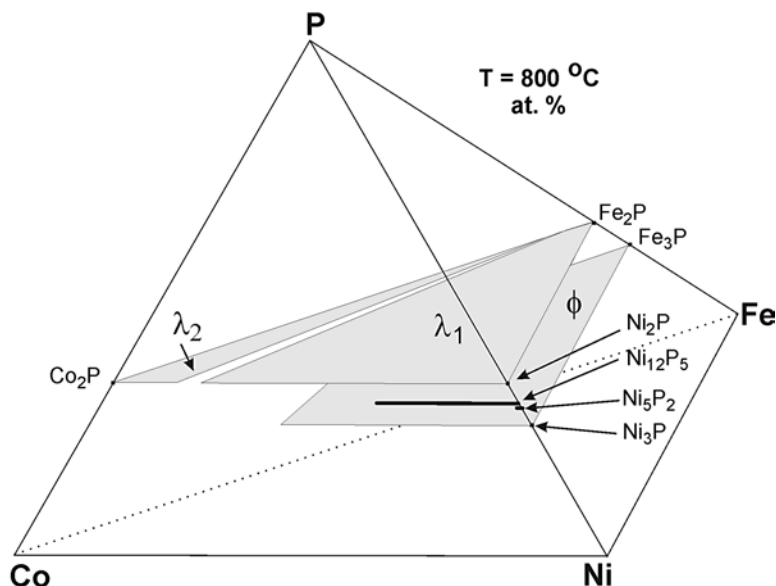


FIG. 1. Solid solutions in the Co–Fe–Ni–P tetrahedron at 800°C. The stoichiometry of the solid solutions is schematic for simplicity.

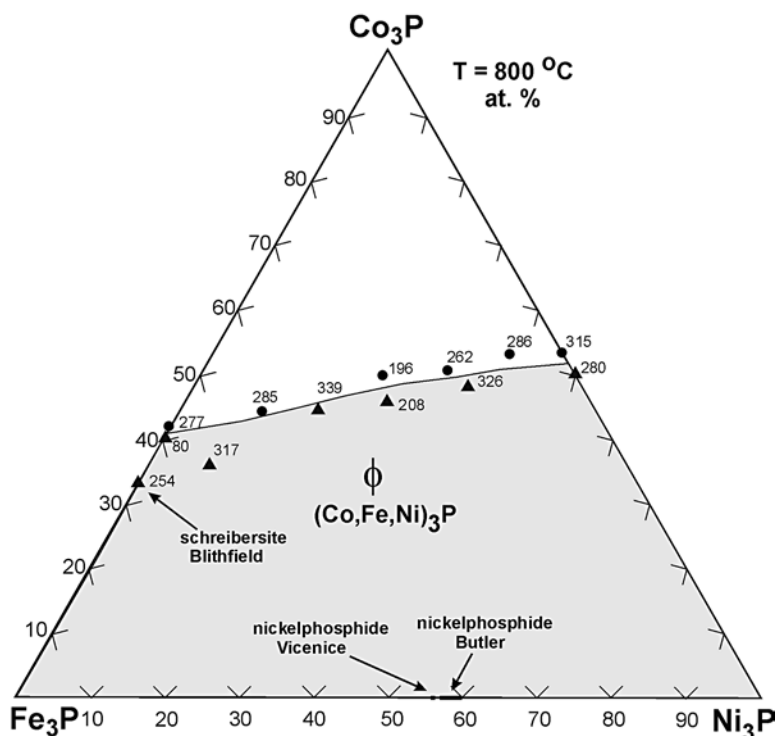


FIG. 2. Phase relations in the pseudoternary system $\text{Co}_3\text{P} - \text{Fe}_3\text{P} - \text{Ni}_3\text{P}$ at 800°C . Symbols: \blacktriangle ϕ $(\text{Co},\text{Ni})_3\text{P}$ solid solution, \bullet quaternary five-phase field.

was focused on $(\text{Fe},\text{Co})_3\text{P}$ and $(\text{Ni},\text{Co})_3\text{P}$ solid solutions. The unit-cell dimensions for the end-members of the ϕ $(\text{Co},\text{Fe},\text{Ni})_3\text{P}$ solid solution are listed in Table 4.

The substitution of cobalt for nickel in the ϕ $(\text{Ni},\text{Co})_3\text{P}$ solid solution is accompanied by practically no changes of unit-cell parameters; the difference between unit-cell volume of the end members is 0.1%. The analogous substitution for iron in $(\text{Fe},\text{Co})_3\text{P}$ solid solution is accompanied by a small decrease in the unit-cell volume, the difference between unit-cell volume of the end members is 1.8%.

The variation of unit-cell dimensions as a function of the Co content is presented in Figure 3. The behavior of the unit-cell parameters of $(\text{Fe},\text{Co})_3\text{P}$ and $(\text{Ni},\text{Co})_3\text{P}$ solid solutions deviates from the Vegard's law, as it does in the $(\text{Fe},\text{Ni})_3\text{P}$ solid solution. There is a linear change, but only for parameter a of the ϕ $(\text{Ni},\text{Co})_3\text{P}$ solid solution, whereas for parameter c and V , this variation is nonlinear. Also the variation of unit-cell parameters a , c , and V of the $(\text{Fe},\text{Ni})_3\text{P}$ solid solution with cobalt content is nonlinear, and a second-order polynomial must be fitted. The unit-cell volume of both end-members of $(\text{Ni},\text{Co})_3\text{P}$ and $(\text{Fe},\text{Co})_3\text{P}$ solid solutions are larger than expected, and also here a second-order polynomial must

be used to describe the variation of unit-cell volume with their Co content.

The pseudoternary system $\text{Co}_2\text{P} - \text{Fe}_2\text{P} - \text{Ni}_2\text{P}$ at 800°C

Based on literature data and on the present experiments, the isothermal 800°C section for the pseudoternary system $\text{Co}_2\text{P} - \text{Fe}_2\text{P} - \text{Ni}_2\text{P}$ is presented in Figure 4. Representative experiments are summarized in Table 5. At this temperature, two solid-solution series are stable, hexagonal $\lambda_1(\text{Ni},\text{Fe},\text{Co})_2\text{P}$ and orthorhombic $\lambda_2(\text{Co},\text{Fe},\text{Ni})_2\text{P}$.

The stability field of the λ_1 solid solution increases distinctly with increasing Ni content. The λ_1 solid solution covers all of the $\text{Fe}_2\text{P} - \text{Ni}_2\text{P}$ join, and on the $\text{Co}_2\text{P} - \text{Fe}_2\text{P}$ join, it reaches up to 8 mol.% Co_2P . Along the $\text{Co}_2\text{P} - \text{Ni}_2\text{P}$ join, the λ_1 solid solution dissolves up to about 75 mol.% Co_2P . The two-phase field $\lambda_1 + \lambda_2$ is narrow and irregular in shape. On the $\text{Co}_2\text{P} - \text{Ni}_2\text{P}$ join, it spans ~ 8 mol.%, and on the $\text{Co}_2\text{P} - \text{Fe}_2\text{P}$ join, it spans ~ 4 mol.% Co_2P .

The stability field of orthorhombic $\lambda_2(\text{Co},\text{Ni},\text{Fe})_2\text{P}$ solid solution is narrow and reaches from about

11 mol.% Co₂P on the Co₂P–Fe₂P join to about 83 mol.% Co₂P along the Co₂P–Ni₂P join.

According to the present experiments, the hexagonal λ_1 solid solution with an Fe:Ni ratio equal to 3 (corresponding to the mineral allabogdanite) is stable with up to at least 14 mol.% Co₂P, and the λ_2 solid solution with the same Fe:Ni ratio is stable up to 30 mol.% Co₂P.

The unit-cell parameters of λ_1 and λ_2 (Co,Fe,Ni)₂P solid solutions vary with composition. The unit-cell

dimensions for the end-members of λ_1 and λ_2 solid solutions are listed in Table 4. An increasing iron content inflates the unit-cell volume of λ_1 (Fe,Ni)₂P solid solution by up to 1.8%. Conversely, increasing cobalt content decreases the unit-cell volume of λ_1 (Co,Ni)₂P by up to 2.3% and of λ_2 (Co,Fe)₂P by up to 3.7%.

TABLE 4. UNIT-CELL DATA FOR THE END-MEMBERS OF THE ϕ (Co,Fe)₃P, ϕ (Co,Ni)₃P, λ_1 (Fe,Ni)₂P, λ_1 (Co,Ni)₂P, λ_2 (Co,Ni)₂P, λ_1 (Co,Fe)₂P AND (Co,Ni)₁₂P₅ SOLID SOLUTIONS

Expt. no.	Composition	<i>a</i> [Å]	<i>b</i> [Å]	<i>c</i> [Å]	<i>V</i> [Å ³]
32/3*	ϕ Fe ₃ P	9.1058(1)	-	4.4605(1)	369.85(1)
P80	ϕ (Co _{0.26} Fe _{0.60}) ₃ P	9.0321(1)	-	4.4514(1)	363.13(1)
P33/3*	ϕ Ni ₃ P	8.9549(1)	-	4.3873(1)	351.82(1)
P280	ϕ (Co _{0.59} Ni _{0.50}) ₃ P	8.9577(1)	-	4.3789(1)	351.37(1)
P255	Ni ₁₂ P ₅	8.6447(3)	-	5.0702(3)	378.89(1)
P256	(Co _{4.8} Ni _{7.2}) ₂ P ₅	8.6107(3)	-	5.0573(3)	374.97(1)
P75*	λ_1 Ni ₂ P	5.8661(4)	-	3.3877(1)	100.96(2)
P164	λ_1 Fe ₂ P	5.8648(7)	-	3.4509(7)	102.79(1)
P165	λ_1 Co _{0.42} Ni _{0.58} P	5.8073(4)	-	3.3797(4)	98.71(1)
P166	λ_1 Co _{0.12} Fe _{1.88} P	5.8650(2)	-	3.4489(2)	102.74(1)
P17*	λ_2 Co ₂ P	5.6474(4)	3.5133(3)	6.6077(5)	131.11(1)
P152	λ_2 Co _{1.67} Ni _{0.33} P	5.6772(2)	3.4973(4)	6.6174(4)	131.38(1)
P193	λ_2 Co _{1.78} Fe _{0.22} P	5.7805(1)	3.5513(1)	6.6338(1)	136.18(1)

* Drábek & Skála (2002).

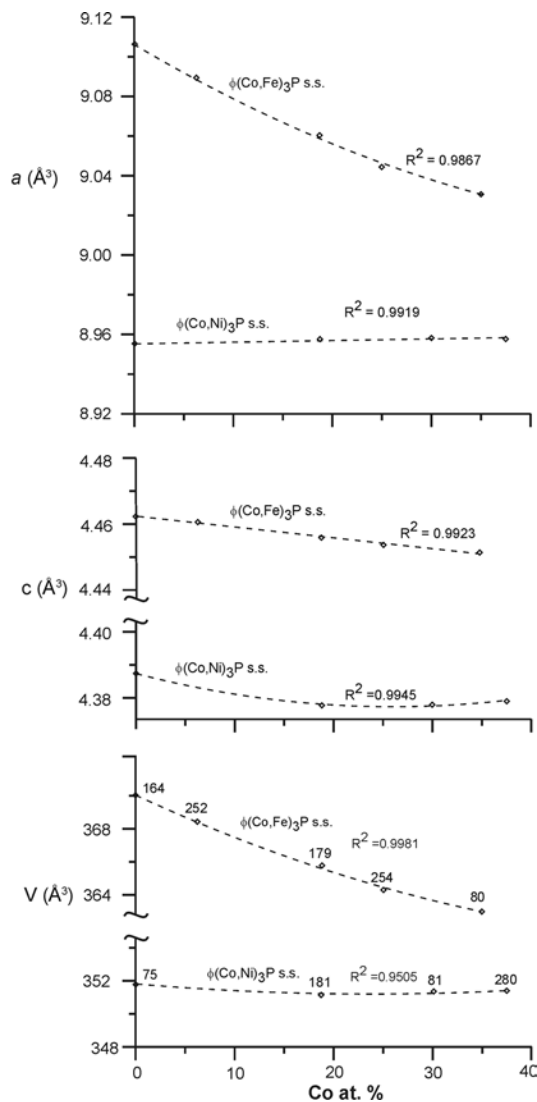


FIG. 3. Variation of unit-cell dimensions of (Co,Ni)₃P and (Co,Fe)₃P solid solutions with their Co content. Symbols indicate results from WPPF. Dashed lines represent the second-order or linear [parameter *c* of (Co,Fe)₃P] fit.

TABLE 5. EXPERIMENTS IN THE PSEUDOTERNARY SYSTEM Co₂P–Fe₂P–Ni₂P PERFORMED AT 800°C

Expt. no.	Starting mixture (mol.%)			Time (hours)	Products
	Co ₂ P	Fe ₂ P	Ni ₂ P		
P90	25.00	50.00	25.00	45	λ_1
P95	80.00	-	20.00	93	$\lambda_1 + \lambda_2$
P118	33.33	33.33	33.33	2512	λ_1
P124	9.09	90.91	-	212	$\lambda_1 + \lambda_2$
P125	50.00	33.33	16.67	210	λ_2
P128	10.00	80.00	10.00	443	$\lambda_1 + \lambda_2$
P129	18.18	72.73	9.09	1147	λ_2
P131	1.94	73.79	24.27	811	λ_1
P134	5.26	84.21	10.53	234	λ_1
P135	16.67	66.67	16.67	234	$\lambda_1 + \lambda_2$
P150	13.04	65.22	21.74	261	λ_1
P151	9.09	72.73	18.18	261	λ_1
P152	83.33	-	16.67	259	λ_2
P156	23.08	61.64	15.38	922	λ_2
P169	71.43	14.29	14.29	95	$\lambda_1 + \lambda_2$
P184	78.43	-	21.57	416	$\lambda_1 + \lambda_2$
P185	20.00	60.00	20.00	498	$\lambda_1 + \lambda_2$
P189	55.56	22.22	22.22	527	$\lambda_1 + \lambda_2$
P190	25.93	55.56	18.52	527	$\lambda_1 + \lambda_2$
P192	14.29	76.19	9.52	527	$\lambda_1 + \lambda_2$
P193	11.11	88.89	-	527	λ_2
P219	29.82	52.63	17.54	330	λ_2
P200	62.30	7.69	23.08	992	$\lambda_1 + \lambda_2$
P221	76.92	7.69	15.38	306	$\lambda_1 + \lambda_2$
P210	35.71	42.86	21.43	513	$\lambda_1 + \lambda_2$
P330	62.50	25.00	12.50	264	λ_1
P338	78.57	14.29	7.14	212	λ_2
P341	7.41	92.59	7.41	449	λ_1
P342	45.45	36.36	18.18	432	$\lambda_1 + \lambda_2$
P345	5.50	13.33	13.33	432	λ_2
P348	74.47	-	25.53	432	λ_1

2002) fall into the experimentally determined field of hexagonal λ_1 (Co,Fe,Ni)₂P solid solution, which occupies the iron-rich corner of the system. However, whereas barringerite is hexagonal, allabogdanite is orthorhombic. Britvin *et al.* (2002) discussed this discrepancy and pointed out the paper of Chenevier *et al.* (1987). The latter authors described high-temperature orthorhombic – low-temperature hexagonal phase-transition of FeMnP at 1473 K. The low-temperature hexagonal FeMnP phase belongs to the Fe₂P structure-type. Also, Ellner & Mittemeijer (2001) described the orthorhombic – hexagonal phase-transition of Co₂P. Orthorhombic, low-temperature α -Co₂P transforms at 1155°C to the high-temperature hexagonal β -Co₂P, isotypic with Fe₂P, a 5.742(2) c 3.457(5) Å. Therefore, it is possible that allabogdanite is a low-temperature polymorph of (Fe,Ni)₂P, and barringerite can be considered as the high-temperature polymorph, in agreement with Britvin *et al.* (2002). Nevertheless, the low-temperature modification of (Fe,Ni)₂P has not been confirmed experimentally.

As demonstrated in Table 4, cell parameters and unit-cell volume depend on the chemical composition of (Co,Fe,Ni)₃P and (Co,Fe,Ni)₂P solid solutions. Generally, iron inflates unit-cell volume of both solid solutions, whereas cobalt has the opposite effect. These changes of the unit-cell volume are in agreement with the ionic radii, which decrease in order Fe, Co, Ni (Mackay *et al.* 1999). Nevertheless, the differences in unit-cell volume are very small and do not offer a possibility of mineralogical application as geobarometers.

According to the recent results, the unit-cell parameters of (Fe,Co)₃P and (Ni,Co)₃P solid solutions, like those of the (Fe_{1-x}Ni_x)₃P solid solution (Skála & Drábek 1999), vary anomalously and depart from Vegard's law. Similarly, recent results confirm the statement of Fruchart *et al.* (1969) concerning the anomalous variation of unit-cell parameters of the (Co,Fe,Ni)₂P solid solution with composition.

The anomalous behavior of the unit-cell parameters of these phosphides may be explained by three non-equivalent sites in the crystal structure and their preferential occupancy, as described by Liu *et al.* (1998), Skála & Drábek (1999), Fruchart *et al.* (1969) and Moretzki *et al.* (2005). Polyhedra around these sites have different volumes (Fruchart *et al.* 1969, Skála & Drábek 1999), and therefore preferential occupancy by

cobalt, iron or nickel may generate the observed anomalous variation in the unit-cell dimensions.

However, in explaining the anomalous behavior of unit-cell parameters of M₂P phosphides, the deviation of stoichiometry of binary phases Co₂P (Rundqvist 1960) and Ni₂P (Lee & Nash 1991) should also be taken into consideration. A detailed crystal-structure investigation is needed to explain the anomalous behavior of unit-cell parameters of 2:1 phosphides. The dependence of site occupancies in 3:1 and 2:1 phosphides on conditions of formation, particularly cooling rates of parent meteorites, requires additional research.

CONCLUSIONS

1) The present experimental study reveals broad ranges of miscibility in the pseudoternary systems Co₃P–Fe₃P–Ni₃P and Co₂P–Fe₂P–Ni₂P. All phosphides known as minerals can be described in terms of these components (Figs. 2, 4).

2) Experiments show that in the pseudoternary system Co₃P–Fe₃P–Ni₃P, the schreibersite structure-type is retained over a broad field outlined by four formulas Fe₃P, Ni₃P, Co_{1.2}Fe_{1.8}P (30.0 at.% Co) and Co_{1.7}Ni_{1.3}P (42.5 at.% Co).

3) Experiments performed in the pseudoternary system Co₂P–Fe₂P–Ni₂P confirm the existence of hexagonal (λ_1) and orthorhombic (λ_2) (Co,Fe,Ni)₂P solid-solutions.

4) According to the experiments performed, the hexagonal λ_1 solid-solution with an Fe:Ni ratio equal to 3, corresponding to allabogdanite, dissolves at 800°C at least 14 mol.% Co₂P, and beyond that it transforms to the orthorhombic λ_2 modification. The solid solution (Fe_{1.5}Ni_{0.5})₂P, chemically analogous to allabogdanite, has a hexagonal structure (*P62m*) with unit-cell parameters a 5.8446(3), c 3.4568(5), V 102.26(1) Å³, $c/a = 0.5915(1)$ (Drábek & Skála 2002). The same run repeated at 400°C also falls in the hexagonal λ_1 solid-solution field.

5) Experiments conducted in the ternary system Co–Ni–P reveal that the phase with composition (Co,Ni)₁₂P₅ forms a stable assemblage with λ_1 (Fe,Ni)₂P and (Co,Ni)₃P. Similarly, (Co,Ni)₅P₂ forms a stable assemblage with (Ni,Co)₃P and (Co,Ni)₁₂P₅. The phases (Co,Ni)₁₂P₅ and (Co,Ni)₅P₂ can be expected to occur in nature in close association with nickelposphide or barringerite.

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TABLE 6. EXPERIMENTS IN THE TERNARY Co–Ni–P SYSTEM AT 800°C

Experiment no.	Starting mixture (at. %)			Time hours	Products
	Co	Ni	P		
P178	-	70.00	30.00	300	Ni ₃ P ₅ + Ni ₂ P
P263	29.41	41.18	29.41	692	Ni ₃ P ₅ + >>Ni ₂ P + λ_1
P320	1.79	69.64	28.57	1000	Ni ₃ P ₅ + >> Ni ₁₂ P ₅
P335	2.51	68.92	28.57	786	Ni ₁₂ P ₅ + Ni ₃ P ₂ + Ni ₂ P?

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