

COPPER-NICKEL ARSENIDES OF THE MOHAWK NO. 2  
MINE, MOHAWK, KEWEENAW CO., MICHIGAN

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ABSTRACT

Copper-nickel arsenides collected from a large fissure at the Mohawk No. 2 mine, Mohawk, Keweenaw Co., Michigan were investigated by powder diffractometry and electron probe analysis. These materials correspond to the "keweenawite" and "mohawkite" of Koenig and the "ledouxite" of Richards. The phases identified include  $\alpha$ -domeykite,  $\beta$ -domeykite, algodonite, arsenical copper, rammelsbergite, pararammelsbergite, and niccolite.

Sealed silica tube studies in the system Cu-Ni-As at  $510 \pm 5^\circ\text{C}$  show negligible solubility of copper in the nickel arsenides and nickel in the copper arsenides. All examples encountered in the Mohawk disequilibrium assemblage appear to involve essentially no (Cu,Ni) solid solubility among the binary arsenide compounds.

There is strong evidence that the nickel arsenides crystallized earlier at higher temperatures, were fractured and subsequently partially replaced by the copper arsenide-bearing solutions at lower temperature. Reaction rims around the nickel arsenides represent products which are consistent with the inferred stability of coexisting phases in the Cu-Ni-As system.

INTRODUCTION

This paper describes and discusses the paragenesis of the coexisting copper-nickel arsenides which comprise the so-called "keweenawite" and "mohawkite" of the Mohawk No. 2 mine, Mohawk, Keweenaw Co., Michigan. Prior to the advent of the techniques of metallography and X-ray diffractometry, a spate of names appeared in the literature including "ledouxite" (Richards, 1901), "keweenawite", "mohawkite" and "whitneyite" (Koenig, 1900). All were eventually stated to be mixtures of at least seven known and unknown phases by Butler and Burbank (1929). Although these authors primarily discussed the copper arsenides, they mentioned the existence of several unknown nickel and cobalt arsenides.

The now-inaccessible Mohawk No. 2 shaft was driven into a member of the Kearsarge Lode series of amygdaloidal basalts and encountered unusually large quantities of copper arsenides, witnessed by the removal of over 230,000 pounds of "mohawkite" material (Butler and Burbank, 1929). A more recent list of copper-nickel arsenides from this general region was published by Williams (1963).

Occurrences of coexisting copper-nickel arsenides are few and include Černý Důl, Krkonoše, Bohemia where arsenic, arsenolamprite, niccolite, koutekite, paxite, and novakite were described by Johan (1962) and the

Talmessi mine, Anarak, Iran from which niccolite, algodonite, and  $\alpha$ -domeykite were identified by Bariand and Herpin (1960).

To assist in the paragenetic interpretation of the Mohawk mine arsenides, the system Cu-Ni-As was investigated at  $510 \pm 5^\circ\text{C}$  by synthesis in evacuated sealed silica tubes.

#### ARSENIDES OF THE MOHAWK NO. 2 MINE

Phases encountered and described include  $\alpha$ -domeykite ( $\text{Cu}_3\text{As}$ ),  $\beta$ -domeykite ( $\text{Cu}_{3-x}\text{As}$ ), algodonite ( $\text{Cu}_{6\pm x}\text{As}$ ), arsenical copper ( $\text{Cu,As}_{s,s.}$ ), rammelsbergite ( $\text{NiAs}_2$ ), pararammelsbergite ( $\text{NiAs}_2$ ), and niccolite ( $\text{Ni}_{1\pm x}\text{As}$ ).

*Specimens.* A representative suite of specimens was gathered in 1962 by the author from the 11th and 12th levels, 200 ft. S.W. of the Mohawk No. 2 shaft. Since then, access to the shaft has been sealed and the neighboring mines with access routes have been abandoned.

The arsenide-bearing fissure pinches and swells, in some places attaining a thickness of four feet, and is nearly completely filled with arsenides and considerable amounts of nearly pure calcite. Recent action by mine waters has produced numerous hydrated calcium and copper arsenates which frequently coat the calcite and the arsenides. In some places, calcite is the sole mineral. A history of brecciation is evident with angular pieces of wall-rock immersed within the calcite. A large stope between the levels exposes the fissure, which shows veins of  $\alpha$ -domeykite up to two feet in thickness. The material in place is of a pale chalcopyrite-yellow color, much like pyrrhotite in appearance; when freshly broken, samples afford the smell of arsine gas. When brought to the surface,  $\alpha$ -domeykite characteristically tarnishes to a chalcopyrite-yellow color and develops within a few years a fuzzy black pulverulent coating not evident *in situ* which consists of at least two phases. One of these phases is pale green in color and yields a complex powder pattern similar to tyrolite, indicative of a product of oxidation. This coating can be observed on nearly all  $\alpha$ -domeykites preserved in collections. It is likely that the presence of reducing mine gases such as methane inhibit the surficial oxidation of  $\alpha$ -domeykite in place.

Knots of greyish tin-white rammelsbergite of botryoidal and fibrous appearance occur in places, usually along the edge of the fissure, and these invariably show tree-like fractures filled with  $\alpha$ -domeykite. Polished sections of the "keweenawite" display rammelsbergite with a reniform or botryoidal outline, mimicking the appearance of the cobalt-nickel arsenides from the Cobalt-Sudbury region in Ontario. Masses up to six inches across consisting principally of nickel arsenides are not rare, but  $\alpha$ -domeykite is by far the most abundant arsenide in the fissure. Pinkish niccolite usually separates the rammelsbergite from  $\alpha$ -domeykite and occurs as thin zones to fairly large masses intimately mixed with rammelsbergite and  $\alpha$ -domeykite.

Often, the centers of the fissure fillings contain  $\alpha$ -domeykite which passes laterally into  $\alpha$ -domeykite-niccolite mixtures which in turn grade into niccolite-rammelsbergite mixtures. Figure 1 represents a typical appearance and shows the tree-like  $\alpha$ -domeykite bordered by niccolite which adjoins the rammelsbergite. These phases can be visually distinguished if the polished sections are allowed to tarnish in air. Rammelsbergite retains its tin-white appearance, niccolite appears brassy-pink, and  $\alpha$ -domeykite assumes an oily-green tarnish. Sometimes these mixtures are so intimately mixed that resolution of the phases is prohibitive—even by probe techniques—and recourse to powder diffractometry is necessary. Although the neighboring large masses of  $\alpha$ -domeykite appear to be consti-

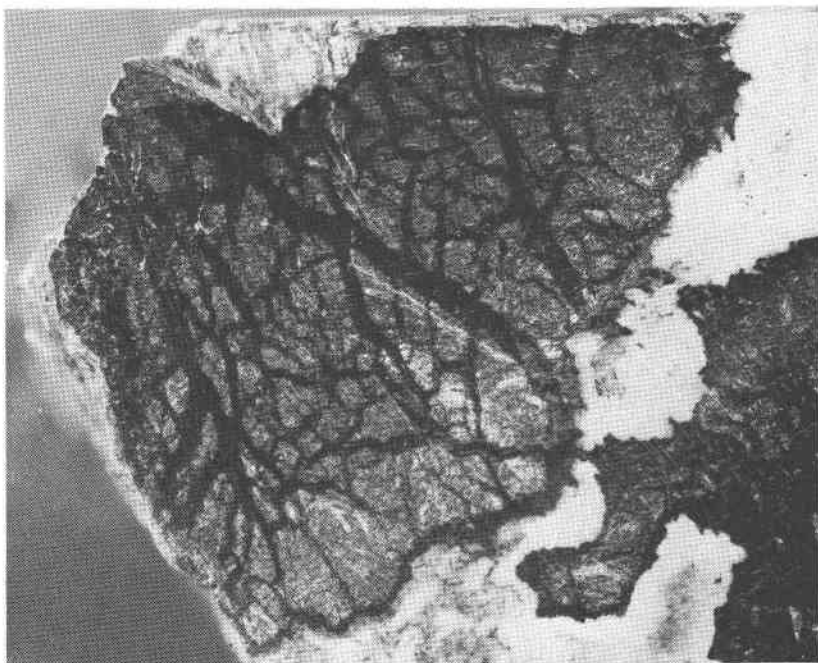


FIG. 1. Photograph of  $\alpha$ -domeykite-rammelsbergite-niccolite mixture which was polished and allowed to tarnish in air. The  $\alpha$ -domeykite appears as the dark tree-like outline, and the niccolite-rammelsbergite mixture is mottled. Occasional islands of pure rammelsbergite are white. The calcite which surrounds the sample and which occurs as rare late-stage veins is white. The sample is about 5 cm. across.

tuted of pure material, rare tiny remnant grains of niccolite, arsenical copper, and algodonite were verified by probe analysis.

These rammelsbergite-niccolite- $\alpha$ -domeykite mixtures reveal a striking resemblance to Koenig's type specimens of "keweenawite" and "mohawkite" which he apparently collected from the same fissure intersecting the 5th level, and the intimate aspect of some of the mixtures doubtlessly led him to conclude that the materials were homogeneous. Koenig's location was inaccessible during the time of specimen collection due to extensive mine collapse.

Less frequent species identified in the course of this study include pararammelsbergite,  $\beta$ -domeykite, algodonite, and arsenical copper. The algodonite and arsenical copper, rare at this locality, are common at some other mines. Enormous masses were once encountered at the Ahmeek No. 3 and 4 mines about a mile to the south and now lay buried in the waste heaps. The  $\beta$ -domeykite is usually intermixed with  $\alpha$ -domeykite; however, a sample collected and kindly donated by G. Kullerud from the adjacent Seneca shaft consists essentially of  $\beta$ -domeykite. Maucherite was not encountered, but it occurs in some fissures at other locations in the Keweenaw Peninsula, usually with algodonite (B. J. Skinner, pers. comm.).

It may be remarked that the relative abundances of the Cu-Ni-As phases encountered

even in one fissure may vary extensively and the assemblage reported herein is representative on only one specific location. However, it is believed that the detailed microparagenesis of the associated phases is essentially repeated at the other arsenide occurrences in the Keweenaw Peninsula since specimens of copper-nickel arsenides from several other locations show the same associations when examined on a small scale.

*Experimental.* ARL electron probe analysis and X-ray powder diffraction studies were undertaken on the natural samples. Studies in the Ni-As system by Yund (1961) and the Cu-As system by Skinner, Adler, and Mead (1963) and Skinner and Luce (1971), and an isothermal section of the Cu-Ni-As system at 510°C, discussed subsequently, were invaluable aids in interpretation of the mineralogical relations.

Koenig's bulk analyses of "keweenawite" and "mohawkite" fall within the  $\text{Cu}_3\text{As}-\text{NiAs}_2-\text{Ni}_{11}\text{As}_8$  field as depicted in Figure 2 and samples investigated in this paper, with rare exception, also fall within this field.

Two kinds of analyses were performed on the electron probe. Matrix absorption and enhancement calculations showed that no corrections were necessary if pure  $\text{Cu}_3\text{As}$  and  $\text{NiAs}_2$  were used as standards. These included chemically analyzed  $\alpha$ -domeykite and rammelsbergite, the latter containing 0.6 percent Co. With the exception of cobalt in the rammels-

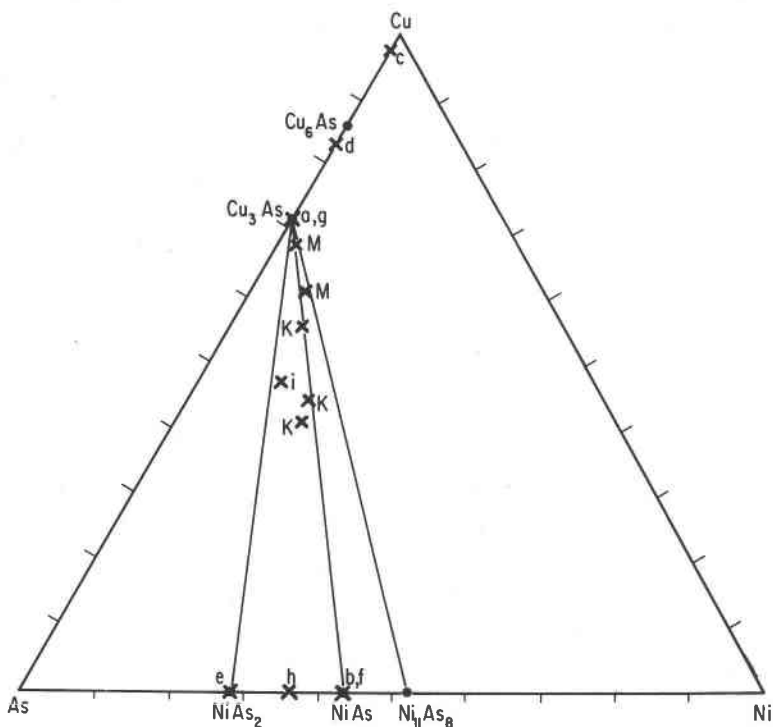


FIG. 2. "Mohawkite" and "keweenawite" samples which have been analyzed. Koenig's (1960) bulk analyses include "mohawkite" (M) and "keweenawite" (K). Analyses a to i appear in Table 1.

Table 1. Electron Probe Microanalyses of Mohawk Cu-Ni Arsenides

<u>Code (see Fig.2)</u>	<u>Visual appearance</u>	<u>Weight %</u>	<u>Species</u>
In $\alpha$ -domeykite			
a	yellowish cream	As: 29.0 Cu: 70.5 Ni: nil	$\alpha$ -domeykite
b	pale pink (small islands)	As: 60.0 Cu: 1.0 Ni: 41.0	niccolite
c	bright pink (small islands)	As: 2.5 Cu: 97.0 Ni: nil	arsenical copper
d	yellowish-white (small islands)	As: 20.0 Cu: 81.5 Ni: nil	algononite
"keweenawite"			
e	creamy white	As: 69.0 Cu: 0.5 Ni: 30.0	rammelsbergite
f	pale pink	As: 56.0 Cu: nil Ni: 42.3	niccolite
g	yellowish cream	As: 28.2 Cu: 71.5 Ni: nil	$\alpha$ -domeykite
h	palest pink	As: 63.6 Cu: nil Ni: 36.0	rammelsbergite and niccolite
i	cream white	As: not run Cu: 45.0 Ni: 11.4	$\alpha$ -domeykite and rammelsbergite

bergite, the standards constituted stoichiometric and pure compounds. Using a 2  $\mu$  beam, the CuK $\alpha$ , NiK $\alpha$ , and AsK $\alpha$  spectra were analysed.

The first set of analyses was based on a polished section of an essentially pure  $\alpha$ -domeykite which constituted a portion of the large arsenide masses (Table 1, a to d) and a polished section of "keweenawite" (Table 1, e to i). The results of the analyses are shown on Figure 2. The second set of analyses consisted of traverses across the  $\alpha$ -domeykite veinlets which cut the rammelsbergite and niccolite, and these results are shown in Figure 3.

Powder diffractographs were obtained for a variety of "keweenawite" and "mohawkite" samples using Ni-filtered Cu radiation and CaF<sub>2</sub> as an internal standard. These mixtures all contained variable amounts of rammelsbergite, niccolite,  $\alpha$ -domeykite,  $\beta$ -domeykite, and parammelsbergite. Two typical diffraction spectra of samples from the second set of probe analyses are offered in Table 2. The spacings were indexed according to the cell orientations presented in the ASTM Powder Data File, 1963.

A sample consisting of the disequilibrium assemblage parammelsbergite, niccolite, and  $\alpha$ -domeykite was finely ground and heated in a sealed silica tube for seven days at

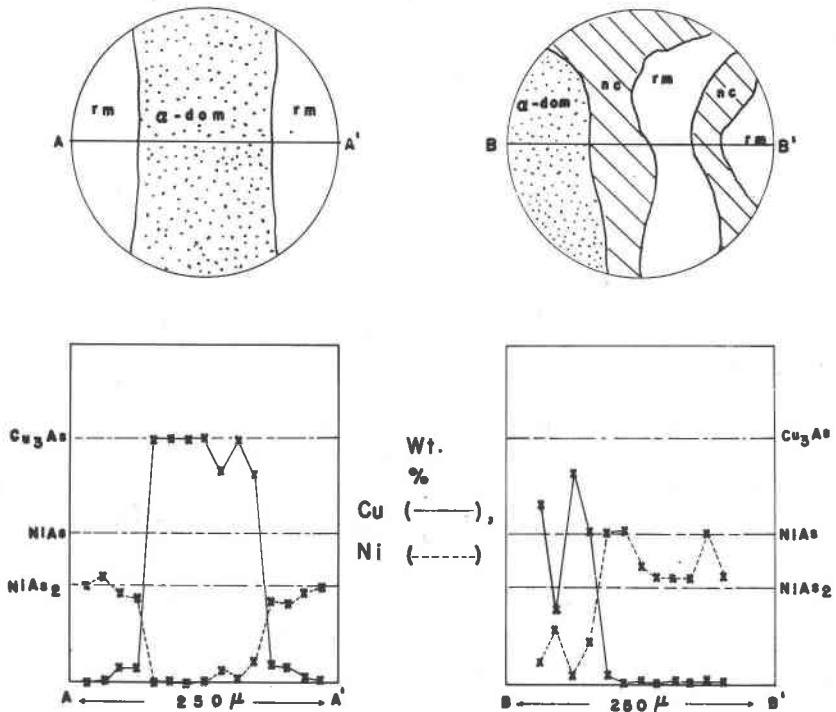


FIG. 3. ARL electron microprobe traverses across "keweenawites" interpreted as weight percentages. Crosses falling off the pure composition lines represent finely dispersed mechanical mixtures.

$510 \pm 5^\circ\text{C}$  in an attempt to determine the upper limit on the pararammelsbergite inversion temperature. Separation of pararammelsbergite from adjoining niccolite and  $\alpha$ -domeykite was prohibitive since the association was intimately mixed. However, the study of the Cu-Ni-As system demonstrates that the presence of copper arsenides and niccolite would have little or no effect on the inversion temperature for the stoichiometric  $\text{NiAs}_2$  dimorphous pair. The appearance of rammelsbergite after heating (Table 3) shows that the inversion temperature of the dimorphous pair is lowered in the Mohawk material since Yund established this inversion for the pure compounds at  $590 \pm 10^\circ\text{C}$  at 1 bar by extrapolation in  $P$ - $T$  space. Since certain other transition elements and Group V and VI elements are known to strongly influence inversion temperatures of arsenides, even if present in relatively small quantities, it is believed that the presence of cobalt in the Mohawk material has contributed to the lowering of the inversion temperature. Extreme sluggishness of the inversion at lower temperatures prohibited determination of a lower temperature limit.

#### A NOTE ON THE Cu-Ni-As SUBSOLIDUS AT $510 \pm 5^\circ\text{C}$

The primary objectives of this experiment were to establish the extent of solid solution of nickel in the copper arsenides and copper in the nickel

Table 2. X-ray Powder Diffractography of "Keweenawite" Mixtures.  
 Cu/Ni radiation,  $\text{CaF}_2$  internal, errors  $\pm 0.003 \text{ \AA}$ .

$I/I_0$	$d_{\text{hk1}}$	hk1	species	$I/I_0$	$d_{\text{hk1}}$	hk1	species
22	2.897 $\text{Å}$	020	nm	15	3.91	112	$\alpha$ -dom
100	2.830	110	nm	7	3.40	022	$\alpha$ -dom
45	2.662	101	nc	28	3.04	013	$\alpha$ -dom
80	2.546	111	nm	69	2.660	101	nc
62	2.477	012	nm	15	2.570	123	$\alpha$ -dom
8	2.152	024	$\alpha$ -dom	5	2.404	004	$\beta$ -dom
25	2.051	233	$\alpha$ -dom	31	2.151	024	$\alpha$ -dom
9	2.024	112	nm	85	2.051	233	$\alpha$ -dom
40	1.9637	102	nc	100	1.9637	102	nc

Table 3. X-ray Powder Diffractography of Unheated and Heated Mohawk Pararammelsbergite.  
Cu/Ni radiation, CaF<sub>2</sub> internal, errors ± 0.003 Å.

Mohawk prm with nc and $\alpha$ -dom				Same material heated for seven days at 510°C and quenched			
$I/I_0$	$d_{hkl}$	hkl	species	$I/I_0$	$d_{hkl}$	hkl	species
44	2.854	004	prm	43	2.854	004	prm
20	2.789	021	prm	35	2.827	110	rm
83	2.660	101	nc	16	2.791	021	prm
42	2.595	022	prm	95	2.662	101	nc
100	2.558	121	prm	32	2.596	022	prm
65	2.522	211	prm	89	2.558	121	prm
40	2.367	122	prm	49	2.540	111	rm
40	2.355	212	prm	54	2.522	211	prm
27	2.151	024	$\alpha$ -dom	22	2.479	012	rm
52	2.051	233	$\alpha$ -dom	40	2.368	122	prm
25	1.9964	221	prm	38	2.359	202	$\beta$ -dom
97	1.9633	102	nc	40	2.355	212	prm
				54	2.053	300	$\beta$ -dom
				70	2.006	113	$\beta$ -dom
				100	1.9629	102	nc

arsenides, the possible existence of some ternary phase or phases and the fields of coexisting phases. Reactions are relatively rapid at about 500°C and since some of the phases pertinent to the Mohawk disequilibrium assemblage persist to this temperature, this isotherm was chosen. It must be emphasized that the natural assemblages were deposited at lower temperatures and contain binary phases not present in this isothermal section. Although limited solid solubility in an ionic system at a higher temperature indicates even less solubility at some lower temperature, the same inference applied to covalently bonded systems such as the arsenides must be used with caution since electronic band states are sensitive to temperature. We note, however, that there does not appear to exist any isotopic pair in the Cu-As and Ni-As systems even at low temperatures, favoring the inference of probable lack of solid solubility if such is the case at higher temperatures.

*Experimental.* Nicke! containing less than 0.03 percent impurities and copper and arsenic each with less than 0.002 percent impurities were used. All experiments utilized evacuated



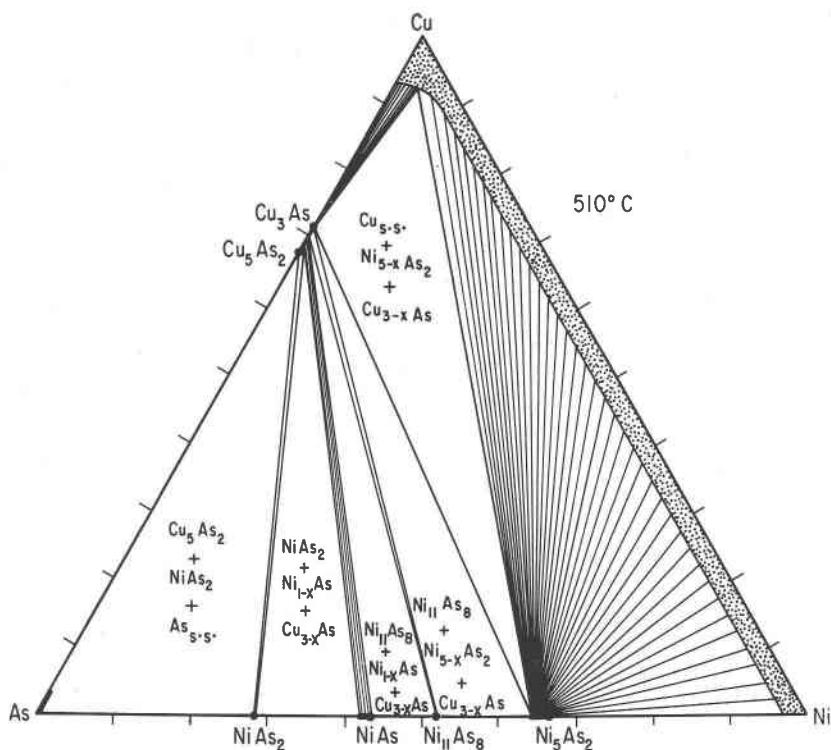


FIG. 4. Interpretation of the Cu-Ni-As condensed system at 510°C. The runs are listed in Table 4.

and sealed silica-glass tubes with a glass rod inserted to tightly pack the charge and to minimize vapor space. The charges were heated at  $510 \pm 5^\circ\text{C}$  for ten days, reground to assure uniform mixing, sealed and heated for six days more, quenched by dropping in ice water, and then examined optically for inhomogeneities. The materials in all experiments appeared to have reacted rapidly and completely. The phases present were then identified by conventional oscillation powder diffraction techniques, employing  $\text{CaF}_2$  ( $a = 5.4626 \pm 0.0005 \text{ \AA}$ ) as the internal standard.

**Phases Present.** The following solid phases were synthesized in these experiments: copper-nickel-arsenic solid solution ( $(\text{Cu}, \text{Ni}, \text{As})_{\text{s.s.}}$ ),  $\beta$ -domeykite ( $\beta\text{-dom}$ ,  $\text{Cu}_{3-x}\text{As}$ ), koutekite ( $\text{ko}$ ,  $\text{Cu}_5\text{As}_2$ ), pararammelsbergite ( $\text{prm}$ ,  $\text{NiAs}_2$ ), niccolite ( $\text{nc}$ ,  $\text{Ni}_{1-x}\text{As}$ ), and maucherite ( $\text{ma}$ ,  $\text{Ni}_{11}\text{As}_8$ ). The essential features of the Cu-Ni-As condensed system at 510°C are shown in Figure 4; the corresponding charges are listed in Table 4.

No ternary phases were encountered throughout this isothermal section. The univariant fields include  $(\text{As}, \text{Cu})_{\text{s.s.}} + \text{ko} + \text{prm} + \text{Vapor}$

Table 4. Syntheses in the System Cu-Ni-As at  $510 \pm 5^\circ\text{C}$ .

Run	Weight %		Phases observed	Comments
	Cu	Ni		
1	5.6	25.2	prm + $\beta$ -dom + ko? + V	ko very minor
2	10.5	20.2	prm + ko + $\text{As}_{\text{s.s.}}$ + V	$d_{102}$ As = 2.769 Å
3	19.9	25.2	prm + nc + $\beta$ -dom + V	$d_{113}$ $\beta$ -dom = 2.005
4	4.7	35.4	nc + prm + $\beta$ -dom + V	
5	10.1	30.0	prm + nc + $\beta$ -dom + V	
6	20.3	20.3	prm + $\beta$ -dom + nc + V	nc very minor
7	40.2	12.4	prm + $\beta$ -dom + V	$d_{113}$ $\beta$ -dom = 2.005
8	47.8	14.7	$\beta$ -dom + nc + V	$d_{113}$ $\beta$ -dom = 2.011
9	29.9	24.4	nc + $\beta$ -dom + V	$d_{113}$ $\beta$ -dom = 2.005
10	10.7	40.3	ma + nc + $\beta$ -dom + V	
11	30.0	30.0	ma + $\beta$ -dom + $\text{Ni}_{5-x}\text{As}_2$ + V	
12	20.2	40.1	ma + $\text{Ni}_{5-x}\text{As}_2$ + $\text{Cu}_{\text{s.s.}}$ + V	$d_{106}$ $\text{Ni}_{5-x}\text{As}_2$ = 1.9719
13	60.0	10.3	$\beta$ -dom + $\text{Ni}_{5-x}\text{As}_2$ + $\text{Cu}_{\text{s.s.}}$ + V	$d_{113}$ $\beta$ -dom = 2.015
14	49.9	20.8	$\beta$ -dom + $\text{Ni}_{5-x}\text{As}_2$ + $\text{Cu}_{\text{s.s.}}$ + V	
15	30.2	40.1	$\text{Ni}_{5-x}\text{As}_2$ + $\beta$ -dom + $\text{Cu}_{\text{s.s.}}$ + V	$d_{111}$ $\text{Cu}_{\text{s.s.}}$ = 2.100
16	20.0	50.3	$\text{Ni}_{5-x}\text{As}_2$ + $\text{Cu}_{\text{s.s.}}$ + V	
17	80.2	3.0	$\beta$ -dom + $\text{Cu}_{\text{s.s.}}$ + $\text{Ni}_{5-x}\text{As}_2$ + V	
18	69.9	10.3	$\beta$ -dom + $\text{Cu}_{\text{s.s.}}$ + $\text{Ni}_{5-x}\text{As}_2$ + V	
19	89.5	5.5	$\text{Cu}_{\text{s.s.}}$ + $\text{Ni}_{5-x}\text{As}_2$ + $\beta$ -dom? + V	$\beta$ -dom very minor
20	80.6	10.1	$\text{Cu}_{\text{s.s.}}$ + $\beta$ -dom + $\text{Ni}_{5-x}\text{As}_2$ + V	$d_{111}$ $\text{Cu}_{\text{s.s.}}$ = 2.103
20a	71.6	0.4	$\beta$ -dom + $\text{Cu}_{\text{s.s.}}$ + V	
20b	67.9	0.2	$\beta$ -dom + ko + V	$d_7$ ko = 2.085
21	49.0	31.6	$\text{Cu}_{\text{s.s.}}$ + $\text{Ni}_{5-x}\text{As}_2$ + V	
22	68.5	20.9	$\text{Cu}_{\text{s.s.}}$ + $\text{Ni}_{5-x}\text{As}_2$ + V	$d_{111}$ $\text{Cu}_{\text{s.s.}}$ = 2.082
23	39.8	40.1	$\text{Cu}_{\text{s.s.}}$ + $\text{Ni}_{5-x}\text{As}_2$ + V	$d_{111}$ $\text{Cu}_{\text{s.s.}}$ = 2.077
24	29.3	49.8	$\text{Ni}_{5-x}\text{As}_2$ + $\text{Cu}_{\text{s.s.}}$ + V	$d_{111}$ $\text{Cu}_{\text{s.s.}}$ = 2.071
25	20.2	59.8	$\text{Ni}_{5-x}\text{As}_2$ + $\text{Cu}_{\text{s.s.}}$ + V	$d_{111}$ $\text{Cu}_{\text{s.s.}}$ = 2.059
26	30.4	59.6	$\text{Ni}_{5-x}\text{As}_2$ + $\text{Cu}_{\text{s.s.}}$ + V	
27	21.6	68.5	$\text{Ni}_{5-x}\text{As}_2$ + $\text{Cu}_{\text{s.s.}}$ + V	$d_{111}$ $\text{Cu}_{\text{s.s.}}$ = 2.050

(V)<sup>1</sup>; ko+ $\beta$ -dom+prm+V; prm+nc+ $\beta$ -dom+V; nc+ma+ $\beta$ -dom+V; ma+ $\text{Ni}_{5-x}\text{As}_2$ + $\beta$ -dom+V; ( $\text{Cu}$ ,  $\text{Ni}$ ,  $\text{As}$ )<sub>s.s.</sub>+ $\text{Ni}_{5-x}\text{As}_2$ + $\beta$ -dom+V. Divariant fields are represented by two thin strips of  $\text{nc}_{\text{s.s.}}$ + $\beta$ -dom<sub>s.s.</sub>+V, and  $\beta$ -dom<sub>s.s.</sub>+( $\text{Cu}$ ,  $\text{As}$ ,  $\text{Ni}$ )<sub>s.s.</sub>+V; and an extensive ( $\text{Cu}$ ,  $\text{Ni}$ ,  $\text{As}$ )<sub>s.s.</sub>+ $\text{Ni}_{5-x}\text{As}_2$ +V field.

In this study, pararammelsbergite is shown to be the stable dimorph and it is inferred that the presence of coexisting copper arsenides has

<sup>1</sup> The vapor pressure of arsenic does not exceed 1 Atm. below 604°C.

Table 5. X-ray Powder Diffractography of Synthetic and Mohawk Rammelsbergite, Pararammelsbergite, Niccolite,  $\alpha$ -Domeykite Assemblages.  
Cu/Ni radiation, CaF<sub>2</sub> internal, errors  $\pm$  0.003 Å.

	$d_{hkl}$	hkl
1. synthetic rm	2.547 Å	111
synthetic rm with $\beta$ -dom (quenched from 650°C)	2.546	111
Mohawk rm with $\alpha$ -dom	2.547	111
2. synthetic prm	2.559	121
synthetic prm with $\beta$ -dom (quenched from 510°C)	2.559	121
Mohawk prm with $\alpha$ -dom	2.559	121
3. synthetic nc with $\beta$ -dom and ma (quenched from 510°C)	2.661	101
Mohawk nc with $\alpha$ -dor	2.661	101

little or no effect on the inversion temperature. Oscillation diffractographs about the  $d_{121}$  reflection of synthetic pararammelsbergite coexisting with  $\beta$ -domeykite prepared at 510°C as well as  $d_{111}$  of rammelsbergite coexisting with  $\beta$ -domeykite at 650°C show no significant differences in their respective  $d$ -spacings when compared with the pure synthetic NiAs<sub>2</sub> dimorphs (Table 5).

Koutekite, Cu<sub>5</sub>As<sub>2</sub>, is the stable copper arsenide phase in the arsenic-rich portion of the diagram and coexists with arsenic, pararammelsbergite and  $\beta$ -domeykite. In the system Cu-Ni-As at 510°C, the koutekite-bearing fields are represented by an extensive ko+As<sub>s.s.</sub>+prm+V field and the thin strip ko+ $\beta$ -dom+prm+V. Thus, koutekite does not coexist with niccolite or maucherite. From the NiAs<sub>2</sub>-Cu<sub>5</sub>As<sub>2</sub> join to the Ni<sub>5-x</sub>As<sub>2</sub> ( $x \sim 0.2$ )-(Cu, Ni, As)<sub>s.s.</sub> join,  $\beta$ -domeykite is the persistent Cu-As phase. Algodonite (Cu<sub>6±x</sub>As) was not encountered since it decomposes at temperatures greater than 300 ± 20°C with composition Cu<sub>8</sub>As to  $\beta$ -domeykite+Cu<sub>s.s.</sub> and  $\alpha$ -domeykite was absent since it decomposes at temperatures greater than 90°C to algodonite and copper deficient  $\beta$ -domeykite, according to Skinner and Luce.

It is inferred that nickel plays no significant role in the decomposition and inversion temperatures of the low temperature copper arsenides since essentially no nickel solid solubility in  $\beta$ -domeykite and koutekite

at 510°C was detected. Indeed, electron probe analyses on the naturally occurring low temperature coexisting Ni-As and Cu-As phases did not afford any evidence for detectable nickel in the copper arsenides or copper in the nickel arsenides. The lower limit of detectability in the analyses is believed to be 0.1 weight percent.

#### DISCUSSION

The presence of cobalt in Mohawk pararammelsbergite does not allow a reliable estimate of the inversion temperature for the naturally occurring pararammelsbergite-rammelsbergite pair. It can be stated that the temperature of emplacement for the nickel diarsenide is certainly below 510°C since the Mohawk pararammelsbergite was experimentally inverted to rammelsbergite at this temperature. Since  $\alpha$ -domeykite is the most persistent Cu-As phase in the fissure, temperatures of copper arsenide emplacement were not in excess of 90°C, assuming low pressures in the natural assemblage. These solutions, furthermore, were apparently low in arsenic content since the arsenic-rich phases like paxite ( $\text{Cu}_2\text{As}_3$ ), novakite ( $\text{Cu}_4\text{As}_3$ ), and  $(\text{As}, \text{Cu})_{s.s.}$  were not observed. The first two were not observed in the studies of Skinner, Adler, and Mead (1963) in the system Cu-As, which may indicate their slow reaction kinetics at low temperatures, possible metastability, or their stabilization only by impurities present in analyses of natural materials such as Ag.

The nickel arsenides, on the other hand, represent phases in the arsenic-rich portion of the Ni-As system. The partial pressure of arsenic was probably too high to allow formation of maucherite ( $\text{Ni}_{11}\text{As}_8$ ) and  $\text{Ni}_{5-x}\text{As}_2$ . The reniform appearance of the rammelsbergite as well as the existence of tree-like fractures filled with  $\alpha$ -domeykite lead to the conclusion that the nickel arsenides were emplaced earlier in more or less open cavities which were later invaded by copper arsenides. Since the bulk composition of these "keweenawite" mixtures fall within the field  $\text{Cu}_3\text{As-NiAs}_2\text{-NiAs}$ , reaction at the rammelsbergite contact by solutions rich in copper and poor in arsenic leads to the formation of niccolite. In certain instances where small fragments appear wholly engulfed by  $\alpha$ -domeykite, reaction led to the complete formation of niccolite which occurs as small blebs in the  $\alpha$ -domeykite masses.

The rarity of algodonite in association with the great masses of  $\alpha$ -domeykite, phases which can coexist at temperatures below 90°C, indicates that the fluids bore copper and arsenic fractions favoring the precipitation of the stoichiometric  $\text{Cu}_3\text{As}$  phase. It is worthy of note that the algodonite bleb in Table 2 (run d) has composition  $\text{Cu}_{4.9}\text{As}$ , which is close to the arsenic-rich composition for an algodonite in equi-

librium with  $\alpha$ -domeykite, according to the phase equilibrium studies of Skinner and Luce (1971) who state the composition  $\text{Cu}_{5.2}\text{As}$ . With the additional source of copper in the adjoining wall-rocks, the precipitation of  $\alpha$ -domeykite would lead to the diminution of the arsenic content in the fluids relative to their copper content, with the subsequent precipitation of algodonite and arsenical copper at a later period.

An objection may be raised that the copper arsenides were in fact derived from the action of initially arsenic-poor fluids upon the nickel arsenides and the adjoining copper in the wall rocks. This appears to be quite unlikely since the relative quantities of nickel arsenides encountered during mining operations throughout the Keweenaw Peninsula were insignificant with respect to the copper arsenides. Another observation which militates against this objection is the observed rim of niccolite between the rammelsbergite and  $\alpha$ -domeykite; this rim is usually very thin, indicative of only limited reaction between rammelsbergite and the  $\alpha$ -domeykite precipitating fluids.

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