ART. XLII.—*On Mohawkite, Stibio-domeykite, Domeykite, Algodonite and some artificial copper-arsenides;* by GEORGE A. KOENIG.

THE knowledge of the existence of copper arsenides in the Keweenaw copper formation is nearly as old as the mining operations in this region themselves. In the matter of occurrence there are two points to be noted: (1) The arsenides are not found in the bedded deposits of native copper, but always in fissures, intersecting the beds. (2) These veins have thus far only been observed in the lower beds, near the foot of the formation to the southeast. Arsenic, however, is found in the smelted and refined copper of all the mines. This element is a minimal amount in the copper from the Great Conglomerate of the Calumet and Hecla mine and becomes a maximum in the copper from the amygdaloid beds of the lower measures, on which the Mohawk, Wolverine, Arcadian, Sheldon-Columbia, Isle-Royale, Atlantic, Baltic, Champion, etc., are located. The Sheldon-Columbia location near the shore of Portage Lake in the village of Houghton was the first mine which furnished copper arsenides, notably domeykite. The larger part of the specimens in collections come probably from this mine. Whitneyite was found in a quartz vein in dark melaphyr, not far from the present Mohawk, but the existence of any copper rock was not suspected at that time at that point. Several masses of domeykite have been found in the drift on the Hancock shore of Portage Lake, very much decomposed, cuprite and arsenates being the chief products. In the spring of 1898 the opening of a new street in East Houghton on the old Sheldon-Columbia location, disclosed a quartz vein containing some foliated domeykite. Many good specimens were gathered and have come into collections. A similar vein has been known for years on the old Huron location, now the southern end of the Isle-Royale property. Algodonite was found in the Pewabic mine, located on the Quincy amygdaloid bed and which lies about 5000 feet higher than the Isle-Royale amygdaloid. In developing the Mohawk property a cross vein at right angles to the copper-bearing amygdaloid was met in December, 1899. This cross vein was from 12 to 15 inches wide when struck, but has since shown very varying dimensions. In a gangue of quartz and calcite the copper arsenides have been found in this vein more abundantly than in any of the locations mentioned above. Early in January Mr. Fred. Smith, Superintendent of the Mohawk mine, sent me a solid piece weighing from 4 to 5 pounds, with the request to make a thorough investigation and report. On January 18th I reported to Mr. Smith that the mineral substance which he had sent me was a new mineral species which I would call *Mohawkite.* Later on I received other material from Mr. Smith in which I identified an antimonial domeykite for which I propose the name *Stibio-domeykite*, and also some very peculiar intimate mixtures of Mohawkite with Whitneyite. It appears that the Stibio-domeykite is the more prevalent of the arsenides, and not the Mohawkite as was thought at the start. The vein has since been traced to the outcrop where it was found to form a ridge owing to the quartz in the gangue.

1. *Mohawkite.*

Physical properties.—Form is massive ; no crystallization of any sort has been observed. The structure is mostly fine granular, sometimes compact. The color on fresh surface is gray with a faint tinge of yellow. Tarnishes very easily, and the tarnish is apt to be ultimately dull purple. A yellow brassy tarnish is brought about by boiling, though in cold water the original color lasts for two days and more. The color is, however, no sure guide for identification. The mineral is very brittle, and owing to the granular structure is not possible to fix the degree of hardness; it is approximately 3·5. Spec. gr. at 21° C. (in boiled water but without corrections) = 8·07, mean of three closely agreeing trials and with perfect material, of which there was plenty,—4.6294 grams were taken.

Chemical properties.—In closed tube gives no sublimate of arsenic; only a slight sublimate of As^2O^3, owing to the air in the tube. The substance melts in the tube at cherry heat, and colors the glass blue if the heating be kept up for a few minutes (Cobalt). In the open tube the reactions are similar but more pronounced owing to the vigorous oxidation. On charcoal in O. F. copious vapors of As^2O^3, odor of arsenic and ultimately a globule of metallic copper. If a fragment of the mineral be placed in a shallow cavity on charcoal, along side of a borax bead of equal size or somewhat larger, and both fused together in the point of the blue flame, so that the metallic globule be exposed to the air, then the borax bead will assume the pure blue color of cobalt. If this treatment be kept up for sometime and a fresh borax bead be taken every minute, then a brown nickel bead will be obtained and finally a blue or red copper bead; thus proving all the metals present except the trace of iron. This test (Plattner's) should be used always in examining metallic arsenides. Thus the mineral contains copper, nickel, cobalt, iron (trace) and arsenic. Boiling concentr. nitric acid dissolves the mineral without leaving a residue, forming first a green, then a murky blue solution (owing to the interference between nickel-nitrate green and cobalt-nitrate red). HCl does not act upon the mineral. The quantitative analysis was made by several methods:

(*a*) Nitric solution made ammoniacal, alcohol added and magnesia mixture. This is not a good method, because part of the nickel and cobalt enter into the magnesium-ammonium arsenate.

(*b*) Nitric solution made ammoniacal, diluted properly and H^2S passed into hot solution to saturation. Filtrate evaporated to dryness, residue oxidized with HNO^3 and magnesium-ammonium arsenate precipitate. Separation of copper from nickel and cobalt by H^2S; separation of nickel and cobalt by nitrite method.

(*c*) Powder fused with nitrate and carbonate of sodium. This gives very good results for arsenic; but for the fine pulverulent condition of the oxides these latter must be carefully handled to avoid loss.

I find that the magnes. amm. arsenate can be heated on the asbestos pad of a Gooch crucible without loss into pyro-arsenate. From four analyses of perfect material I obtain

Cu	61·67
Ni	7·03
CoO	2·20
Fe	trace
As	28·85
	99·75

hence the atomic ratio

Cu	0·9803		
Ni	0·1200		
Co	0·0373		
	1·1376	2·958	(Cu, Ni, Co)^3
As	0·3847	1·000	As

This is an exact ratio of 3 : 1, the ratio of domeykite. I look upon this as a case of isomorphic replacement. We may expect to find all gradations of replacement within the ratio of 3 : 1. Synthetic experiments lead me to consider this ratio as representing an especially strong one, as of bonds well satisfied; because I have been enabled to obtain it artificially in well defined crystals, of which more hereafter. The molecule Cu^2As is the strongest of all, the other ratios seem to partake more of the nature of alloys, of unsatisfied bonds. It may be urged that a mechanical mixture of the copper arsenide with nickel-cobalt arsenide is here presented. Against such a view speaks the physical condition of the substance in the first place and also that a ratio of $(Ni, Co)^3As$ has not been observed so far. The question presented itself at once as to whether any of the domeykite occurrences in Houghton Co. contain nickel and cobalt. Winkler gives this metal in the Zwickau occurrence at 0·44 per cent. F. A. Genth does not mention it, and even from the Michipicoten Island location where niccolite accompanies it, the nickel is absent in the domeykite. I have examined every accessible specimen qualitatively. Neither nickel nor cobalt could be found by Plattner's test; but nevertheless it is very probable that all domeykite contains both metals in traces, as my careful analysis of the mineral from the Sheldon-Columbia location, both old and recent, demonstrates. From 0·5 gram of substance just sufficient cobalt oxide was obtained to give color to 50 mg. of borax glass and the nickel was proved by reducing the bead with tin on charcoal. Another matter engaged my attention at once, namely the discrepancy in the specific gravities given by the several authors and recorded on page 44, Dana Min., 6th edit. These densities vary between 6·70 and 7·547 against my determination of 8·07 for the Mohawkite. The collection of the Michigan College of Mines contains one fine specimen of domeykite from the Sheldon-Columbia mine. The material is very uniform, a few specks of calcite the only visible gangue. Of this 3·8559 grams were selected. The specific gravity at 21° C. was found = *7·9486*. The whole material was then dissolved, no residue was left and in a part of the liquid calcium was looked for, but only a trace was found. Hence we have every reason to take this specific gravity as that belonging to domeykite; the figures in the literature must be wrong. It is true that the analysis of this substance does not agree with the theoretical composition exactly, namely:

Cu	74·00	Spec. gr. found	7·9486
(Fe, Ni, Co)	0·06	" calculated	8·1020
As	26·14		
	100·20		

Now if we assume that the elements in this combination possess the same specific gravity as they do in the free state, we may calculate the specific gravity. If specific gravity of Cu = 8·96 and of As = 5·63 then the above composition must weigh 8·96×74·00+5·63×26·14 = 8·1020. The specific gravity of the theoretical Cu^3As will be = 8·017. For Mohawkite the calculated specific gravity will be, taking Co = 8·96 and Ni = 9·5 (the highest number on record):

Cu = 61·67 × 8·96 = 5·5256
Ni = 7·03 × 9·5 = 0·6678
Co = 2·02 × 8·96 = 0·1809
As = 23·85 × 5·63 = 1·6242

7·9985
8·0650 found

+0·0665 difference

This is quite a satisfactory agreement. Yet it occurred to me at this stage of the investigation to verify the relations between specific gravity and composition by artificial compounds and also to see in how far domeykite might be obtained in crystals.

A combustion tube was closed at one end over the lamp. Resublimed arsenic, roughly powdered, was placed into the bottom to the amount of 7·9 grams. On top of this was poured 20·0 grs. of copper filings. The latter had been the end product in a determination of oxygen in refined copper. Total non-copper in this material 0·07 per cent, consisting of arsenic and iron. An asbestos plug was put over the copper and the tube placed in horizontal position into an Erlenmeyer combustion furnace. The copper was first heated to a dull cherry redness and then the arsenic was heated to the sublimation temperature. The heating was kept up for two hours, the open end of the tube being provided with a mercury valve to prevent any air currents from entering the tube. The copper absorbed the arsenic with avidity. One could see that only the part nearest the vapors changed in color and 30 minutes from the beginning this front portion began to melt off. After all the arsenic had become volatilized and a considerable part of the liquid compound had been formed the temperature of this liquid was raised to bright redness and kept so until the end of the experiment; it being 6 o'clock P. M. The tube was inclined so that the liquid covered the solid portion and left to cool slowly. In the morning three distinct substances were found. A dark colored fused mass, then a porous gray part and then the apparently unaltered copper filings, merely slightly caked together. (*a*) The dark, fused portion. On the fracture blue-gray color; strongly developed radial structure and, in fact, so closely resembling chalcocite that one could not tell by the eye one from the other. The weight of all three parts was 27·27 grams. The weight of the unaltered (apparently) part was 9·65 grams; hence in the altered part there must be approximately 10·35 of copper and 7·2 grams of arsenic, giving an atomic ratio of 9·6 : 16·4. Now if the quantities taken of copper and arsenic were in the ratio of 3 : 1 it is evident that at red heat the two elements form the compound Cu^2As, leaving much copper unaffected. The specific gravity of this fused arsenide was found at 7·71, (3·8837 grams being taken). The analysis gave

		Calculated for Cu^2As.	
Cu	63·30	Cu	62·69
As	37·00	As	37·31
	100·30		100·00

The calculated specific gravity is = 7·754, giving a minus difference of 0·044 against the actual specific gravity.

(*b*) The porous zone between *a* and the unaltered copper. An ordinary lens showed that this mass consisted of groups of minute crystals, exhibiting very brilliant faces. A power of 50 diameters differentiated the crystals easily. They appear to be combinations similar to those of arsenopyrite. Believing that I had found the method by which these crystals could be prepared readily I destroyed them before making an attempt at measurements, leaving only one group, and this one was lost clumsily. There are still crystals on the copper cylinder showing the forms and building up of the grape-like bunches but I do not consider them worth the trouble connected with micro-goniometric work. 253 milligrams of these groups, which separate easily from the base, were taken for analysis and only the copper was determined, as there could not be anything but it and arsenic in the material. Found

$$Cu = 71{\cdot}39\text{; theoretical for } Cu^3As = 71{\cdot}6\ Cu$$

No doubt can exist as to the identity of these crystals with domeykite. I have made several attempts since to get the crystals but evidently did not hit the right temperature again. I obtained domeykite as crystalline mass. In one experiment I melted together 28·886 grams of the Cu^2As with 7·8 grams of copper in a glass tube. Liquidity maintained for one hour. After cooling the column was found of varying composition from bottom up. The bottom portion showed a fracture similar in color and structure to white iron, with a faint yellow, in fact it looks exactly like the domeykite of Houghton Co. Specific gravity = 8·05 ; percentage of copper = 75·4, considerably above the ratio Cu^3As ; calculated specific gravity=8·085.

Above this was found a laminated or scaly zone, resembling some of the recently found domeykite from Sheldon location. It gives copper = 71·14, very close to Cu^3As.

The top portion resembles in color and structure (very fine grain) the Cu^2As. It gives copper = 64·8.

2. *Stibio-domeykite.*

With this name I propose to designate the domeykite from the Mohawk mine, Keweenaw Co., and any other locality where mineral of similar composition will be found. In physical properties it is undistinguishable from the domeykite of the Houghton Co. mines. It is remarkable for the massiveness of its occurrence, the freedom from admixtures. It has a decided subconchoidal fracture and takes on a brass tarnish very soon, which, however, ultimately turns into bluish purple. It is very brittle but not as friable as the Mohawkite. Its hardness is very near 4, a little below.

Specific gravity at 21° C.= 7·902 (made with 4·5595 grams) B. B. In the open tube after heating the molten globule for five minutes one observes the forming of yellow spots near the globule and a slight ring or patches farther on, which turn yellow on applying higher heat and volatilize in part. Farther on there is a copious sublimate of arsenic trioxide. If now one washes out the tube in a jet of water and passes H^2S into the tube one observes the above ring and patches turn red, whilst the arsenic oxide turns gold-yellow. I was astonished myself to find that one could demonstrate thus the presence of 0·1 per cent antimony in the mineral. On charcoal blow the point of the oxidizing flame upon the melting mineral for two minutes, then drive off the white arsenic with a gentle flame, the antimony trioxide remains. The open tube reaction is preferable and certain. Concentrated nitric acid does not dissolve the mineral completely; a white cloudiness or a white sediment will be left. When fused on charcoal alongside of a borax bead, the latter colors greenish after several minutes' action (cobalt and nickel cannot be thus found, though present in small amount).

The analysis gave (type specimen):

Cu	72·48
(Fe, Ni, Co)	0·24
As	26·45
Sb	0·78
	99·95

This is evidently a typical domeykite, and one would expect likewise that the percentage of antimony is variable. In order to ascertain this I took twelve pieces, all over one pound each, and treated one gram of each with 10^{cc} of concentrated nitric acid, boiling until the color was blue, then added 15^{cc} of water to each and stood the beaker glasses in a row. (The type specimen with its 0·78 antimony was among the lot.) It appeared that all contained antimony, but no two an equal amount. Some showed more, some less than the type specimen. I selected the one with the heaviest sediment and determined the antimony as trisulphide. It gave Sb = 1·29. This must be taken as the maximum until other tests show greater amounts. The Houghton domeykites show no trace of antimony.

3. *Mohawk Whitneyite.*

With this name I shall designate not a species, nor even a variety but simply a most intimate mixture of the two species Whitneyite and Mohawkite, of which considerable masses are at present encountered in the Mohawk mine. This material is distinguishable at once to the layman even. It is very tough and approaches Whitneyite in that respect. Ordinary blows with the hammer fail to break the masses, the chisel is often required and the hammer leaves a dent as in soft metal. The fresh fracture is gray, fine granular, even hackly. These fractures assume a dull brown or olive-green tarnish, much like algodonite and Whitneyite. There are, of course, all gradations, from nearly pure Mohawkite to nearly pure Whitneyite. The material looks homogenous, but is not, as the following analyses show. The samples were broken with the chisel in close proximity to one another.

No. 1.		No. 2.	No. 3.		No. 4.	
Cu	85·36	83·61	Cu	79·36	Cu	84·86
(NiCo)	0·32		Co	0·82	(Ni+Co)	0·64
(by diff.) As	13·59		Ni	0·61	As	13·06
CaCO^3	0·73		Fe	0·36	$(\mathrm{CaMg})\mathrm{Co}^3$	0·71
			As	15·07		
	100·00		CaCO^3	2·41		99·27
			MgCO^3	0·60		
				99·23		

A notable fact is that in No. 3 the cobalt exceeds the nickel. Calcite is the gangue of this material. All manner of atomic ratios can be calculated from these analyses.

No. 1 has the ratio $\mathrm{Cu}^{7.5}$ As
No. 2 " $\mathrm{Cu}^{6.7}$ As
No. 3 " $\mathrm{Cu}^{6.45}$ As
No. 4 " $\mathrm{Cu}^{7.7}$: As

In connection with these results, attention may be called to a communication made by Mr. J. Stanton, Secretary of the Mohawk Mg. Co., to the Engineering and Mining Journal of April 7, 1900. Mr. Stanton here gives Dr. Ledoux's report upon some of the Mohawk mineral. Dr. Ledoux figures from his analysis the ratio Cu$_4$As (including Ni+Co) and says that with this formula Mohawkite will probably be accepted by science. If this ratio does exist then it is *not* Mohawkite; for this name was given by me to Cu^{3}As (including Ni+Co). But the following sentence regarding the material induces me to believe that it was a mixture of Mohawkite and Whitneyite. The report says: "The sample was pulverized and concentrated by washing until under a powerful glass no other minerals were present. Thus purified the mineral was analyzed with the following result: Cu = 68·6; As = 22·67; Ni = 6·55; Co = 1·2; Fe = 0·23; S = 0·53. The sulphur and iron are impurities [why? if the powerful glass showed no other minerals present? Koenig] and it is also reasonably probable that the nickel and cobalt are mechanically mixed in the sample, although it is possible that some of the copper has been replaced by nickel and cobalt." How can Dr. Ledoux calculate a formula at all if he holds such views as here expressed? He gives the specific gravity at 7·8, but as I have shown above, a composition such as he finds must have a higher specific gravity even than I find for the Mohawkite proper, namely 8·140, leaving out both iron and sulphur. The atomic quotients of Dr. Ledoux's percentages are:

Cu	1·089	As	0·302
Ni	0·111		
Co	0·020		
	1·220		

giving the ratio of 4:1, but if nickel and cobalt are thrown out the ratio is nearer 3 : 1 than 4 : 1.

Under the existing conditions I permit myself to doubt the existence of a molecule (Cu, Ni, Co)^{4}As and merely present the facts to the mineralogical public.

4. *Algodonite.*

This species has not yet been observed at the Mohawk mine, though some of the Mohawk-Whitneyite resembles it very much. I was induced to bring it within the present investigation merely by the specific gravity, which is given by Dr. F. A. Genth as the only authority at 7·62. To Dr. Lucius Hubbard I am indebted for the material. This gentleman possesses a handsome specimen from the find at the Pewabic mine, many years ago. The specimen looks like the segment of a nodular piece. It showed the chocolate-brown dull tarnish. But the fresh fracture is beautiful. It has a color and texture exactly like razor-steel. Although very tough, it does not dent like Whitneyite. The nodule was covered with Whitneyite and this mineral shows on Dr. Hubbard's specimen like a thin fringe around the algodonite. I could break off some 5 grams of faultless material. The specific gravity was found at 21° C. = 8·383 (using 3·8418 grams). The analysis made with 0·5 gram. Of silver I could find no trace. The analysis gave

		for Cu^6As	
Cu	83·72	Cu	83·5
(Fe, Ni, Co)	0·08		
As	16·08	As	16·5
	99·88		

Calculated from these figures, the specific gravity is 8·406. This gives a minus difference of 0·023 from my experimental value of 8·383.

Michigan College of Mines, June, 1900.