VIOLARITE AND OTHER RARE NICKEL SULPHIDES*

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Introduction

This paper is in large measure a sequel to one by Buddington describing the nickel minerals of certain localities in southeastern Alaska.[1] Buddington found that in all of the nickel-bearing localities examined, the mineral associations are almost identical and that they bear a close resemblance to those at Sudbury. The inclosing rock is basic, usually a fresh, relatively coarse-grained gabbro. The ore minerals replace the rock minerals. Pyrrhotite predominates; chalcopyrite is always present and in places is relatively abundant; the chief nickel mineral is pentlandite. These three minerals are approximately of the same age. In addition, in most of the localities cited, there is a violet-colored nickel-iron sulphide which replaces pentlandite. The replacing mineral occurs as tiny veinlets following cleavages and other cracks in pentlandite and along the boundaries between pentlandite and the other ore minerals. The appearance of these veinlets is almost identical with that of supergene chalcocite replacing chalcopyrite, bornite, and other hypogene minerals. Buddington concludes that the violet-colored mineral is supergene. He notes the difficulty in isolating the mineral for analysis and refers to it in his paper as "nickel mineral X."

About the same time, Lindgren and Davy published a description of the Key West nickel mine, Nevada.[2] They note the same relationship; a violet-colored nickel mineral replaces pentlandite in structures which convince them that the violet mineral is supergene. They compare this mineral with a violet-colored nickel

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[1] Buddington, A. F., Alaskan Nickel Minerals. *Econ. Geology*, vol. **19**, pp. 521–541, 1924.

[2] Lindgren, W. and Davy, W. M., Nickel Ores from Key West mine, Nevada. *Econ. Geology*, vol. **19**, pp. 309–319, 1924.

sulphide from the Vermilion mine, Sudbury, Ontario, which for many years has been described as polydymite, and they conclude that the two minerals are identical. They question the identity of the Sudbury mineral with polydymite and conclude that it is a new mineral. They propose for it the name violarite in consideration of its violet color, and assign to it the provisional formula NiS_2. Before publishing his own paper, Buddington examined the Key West specimens collected by Lindgren and Davy and found that the violet-colored mineral from Key West was identical with nickel mineral X. He is not convinced, however, that nickel mineral X, and the Sudbury violarite are identical.

In addition to the Alaskan localities, Buddington describes nickel ores from the following localities; Dracut, Mass., Pigeon Point, Minn., Gap, Pa., and the Friday mine, Julian, Cal. In all of these except the Friday specimens, nickel mineral X replaces pentlandite in structures indicating a supergene origin.

The present authors obtained additional material from Sudbury, Ont., the Emory Creek mine, Yale, B. C., and the Floyd County nickel mine, Virginia. In addition Prof. Buddington very kindly placed at their disposal, his entire collection of nickel ores including specimens and polished sections.

A very complete suite of some 200 polished sections of ores from Sudbury, collected by Wandke and Hoffman[3] was also studied. This collection was presented by them to the Laboratory of Economic Geology, Harvard University.

The microscopic examinations and preparations of the samples for analysis were made by Mr. Short and the chemical analyses of violarite were made by Mr. Shannon.

Violarite, $(Ni, Fe)_3S_4$ at Sudbury

Occurrence. The Vermilion mine, Sudbury, is not of great economic importance and its total production is insignificant in comparison with the great Creighton and Frood mines.[4] It has not been in operation for several years. It is, however, noted for its unusual mineral association and as the place of discovery of two new minerals, sperrylite, $PtAs_2$ and violarite. Other minerals noted are chalcopyrite, bornite, chalcocite, and millerite. The pres-

[3] Wandke, Alfred and Hoffman, R., A study of the Sudbury ore deposits. *Econ. Geology*, vol. **19,** pp. 169–204, 1924.

[4] Report of the Royal Ontario Nickel Commission, Toronto, **1917,** p. 155.

ence of pentlandite in Vermilion ores has been reported by several authors. None of the specimens examined by us contains pentlandite, and it is probable that this mineral has been confused with millerite which it resembles. Another peculiarity of the Vermilion ores examined by us which appears significant is the total absence of pyrrhotite. Whether pyrrhotite is present at all in Vermilion ores we are not prepared to say, but the presence of violarite seems to exclude the presence of both pyrrhotite and pentlandite in these ores.

Violarite in Vermilion ores occurs as nodules and irregularly shaped areas in chalcopyrite. Where any relationship between the two minerals can be observed, chalcopyrite is later than violarite. (See Fig. 6). Surrounding the violarite areas are zones of millerite, NiS. The boundary between millerite and chalcopyrite is sharp; between millerite and violarite it is hazy and irregular. (See Figs. 5 and 7). In some areas only faint tinges of violet and the remnants of an inherited cubic cleavage reveal the "ghosts" of the replaced violarite. In other sections millerite replaces violarite in irregular veinlets traversing the violarite areas (Fig. 9). The evidence is conclusive that millerite is later than violarite, and the structures shown by the two minerals indicate that the replacing mineral is supergene.

Violarite is distinctly earlier than quartz. Figure 9 shows well formed quartz prisms of hexagonal and triangular cross-section. These quartz crystals align themselves along the cleavage cracks of violarite and several even retain the cleavage of violarite. If this violarite is supergene, than the quartz which is of later deposition must likewise be supergene. It is known that quartz is deposited by cold solutions but this type of quartz tends to form exceedingly fine interlocking grains, such as the structure at chert. Well formed hexagonal prisms formed by replacement of least suggest, if not prove, deposition by thermal solutions. As already mentioned chalcopyrite, which is the principal mineral in the Vermilion, is later than violarite. Chalcopyrite is hypogene in the ores of the principal mines at Sudbury, and there is no evidence that it is not also hypogene in the ores of the Vermilion mine.

There is one possibility which might explain the Vermilon violarite as of supergene origin, namely, that violarite replaced pentlandite and that the replacement was carried to completion, leaving no remnants of unreplaced pentlandite. Pentlandite is the chief

nickel mineral at Sudbury and it is surprising to find it absent in any nickel ores from that locality. In studying the ores from Gap, Pa., and from the Admiralty mine, Alaska, nickel mineral X replaces pentlandite and the replacement is so complete, that unreplaced areas of pentlandite are hard to find.

On the other hand violarite occurs in two other Sudbury mines, the Levack and the Worthington, and individual specimens where violarite is present, pentlandite is completely absent. And yet pentlandite is the principal nickel mineral in both mines but violarite is absent in specimens containing pentlandite. The inference is that unknown conditions of very limited extent caused the elements to precipitate locally as violarite rather than as pentlandite.

Again, supergene sulphide enrichment is rarely complete. Inspection of polished sections of sooty chalcocite ores of Ducktown, Tennessee, where enriching conditions were most intense will always reveal remnants of unreplaced pyrite, chalcopyrite and sphalerite. At Sudbury, on the other hand, oxidation and enrichment were feeble at best. The country was intensively glaciated in geologically recent times, and hard massive sulphides can be seen outcropping at the surface. Hence, if Sudbury violarite were due to supergene replacement of pentlandite, it would be expected some of the specimens would have some remnants of unreplaced pentlandite. On the contrary, as already stated, pentlandite and violarite are mutually exclusive in the Sudbury specimens examined by us.

Could the cubic cleavage, now seen in violarite, have been inherited from pentlandite, likewise an isometric mineral? This possibility is very slight. Pentlandite has a rough cubic cleavage, often not observed. Violarite has a perfect cubic cleavage, almost equal to that of galena. (Figs. 9 and 10). It is certain that the cleavage now seen in violarite is a property of that mineral.

For the above reasons the authors conclude that the Sudbury violarite is hypogene.

The presence of violarite in the Levack and Worthington ores was first noted by Wandke and Hoffman. In both mines the violarite was obtained at relatively shallow depths. The proportion of specimens containing violarite to the total number of specimens collected by them from these mines is very small and the presence of the violarite was not revealed until the ores were studied under

the microscope. The violarite-bearing ores from the Levack and Worthington contain pyrrhotite, although only sparingly; on the other hand in pentlandite-bearing ores from these mines, pyrrhotite is abundant.

PHYSICAL PROPERTIES AND COMPOSITIONS OF VIOLARITE. Violarite under the reflecting microscope is distinctly violet in ordinary (unpolarized) vertically reflected light. In some of the Sudbury specimens the mineral is isotropic in polarized light; in other specimens the areas between isometric cleavage cracks appear as small interlocking grains of weak anistropism and diverse optical orientation. This strongly suggests that violarite deposited as an isometric mineral but some areas either inverted on cooling or underwent some small chemical alteration resulting in a mineral of lower symmetry.

The etch tests on the polished section are as follows: HNO_3–slowly effervesces and stains brown to black; HCl–no effect on surface but drop turns yellow or green; KCN, $FeCl_3$, KOH, $HgCl_2$–all negative.

Violarite was discovered in the Vermilion mine early in the history of Sudbury and was analyzed by F. W. Clarke and Charles Catlett in 1889.[5] Their analysis after calculating the copper present as chalcopyrite is as follows:

|	
S	41.35
Ni	43.18
Co	. . .
Fe	15.47
	100.00

From this they derived the formula Ni_3FeS_5 and considered that the mineral is identical with polydymite whose formula as given in all texts is Ni_4S_5.

Their work, however, was done before the advent of the reflecting microscope and they did not recognize the presence of millerite, hence their analysis is too high in nickel.

The present authors secured from the U. S. National Museum a specimen of Vermilion ore in which the violarite occurs as nodules up to 0.5 cm. diameter (see Figs. 5–7). Millerite surrounds the

[5] *Am. J. Sc.*, (3) vol. **39**, p. 373, 1889.

nodules but is not included in them. Ten polished sections of this specimen were prepared. Under microscopic observation these were scratched with a No. 6 Sharps needle, and a crater-like cavity was gouged out of each violarite nodule and the powder collected. Care was taken not to overlap the violarite boundaries into the surrounding millerite and chalcopyrite nor to dig so deeply as to penetrate beneath the nodules. When all the powder that could be collected from these 10 specimens was obtained, new surfaces were ground on the sections, care being taken to grind below the craters already gouged out. The surfaces were then re-polished and scratched with the needle as before. This process was continued until the material from 40 polished sections was obtained. It was found that a sharp needle caused the fragments to fly over the surface and it was difficult to prevent the needle from slipping over the boundaries of the violarite. This difficulty was removed by grinding off the end of the needle by holding it against a rapidly revolving carborundum wheel, the axis of the needle forming an angle of about 70° with the surface of the wheel. In this manner a surface of elliptical cross-section was formed at the end of the needle, the former point being a frustum of a cone as shown in
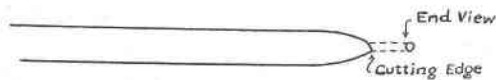
Enlarged View of Needle

sketch. The lower or protruding edge of the needle was pushed downward and into the violarite areas, the powder being shoved just ahead of the needle and reposing at the far edge of the cavity.[6] The best results are obtained by working the needle back and forth and if necessary rotating it slightly to jar loose the mineral particles.

The material thus obtained weighed approximately 0.25 gm. It was passed through a 100 mesh screen, and the gangue was re-moved by floating in methylene iodide. The part which sank was carefully washed, dried and examined under a binocular micro-scope. A few particles of chalcopyrite were observed, otherwise the material appeared to be pure violarite.

[6] The needle was held in a needle-holder with an adjustable chuck; this needle-holder can be obtained from dental supply firms for approximately eighty cents.

The analysis gave the following results and ratios:

		Ratios	Ratios after calculating Cu as $CuFeS_2$
Insoluble	0.40	....	....
Nickel	38.68	.659	.659
Cobalt	1.05	.018	.018
Copper	1.12	.017	....
Iron	17.01	.305	.288
Sulphur	41.68	1.300	1.266 1.266 = 4 × .317

$.965 = 3 \times .322$ (for Nickel, Cobalt, Copper, Iron group)

99.94

Calculating the copper present as chalcopyrite ($CuFeS_2$) the formula obtained is $(Ni, Fe)_3S_4$. The ratio of nickel to iron is approximately 2:1. which would yield the formula $FeS \cdot Ni_2S_3$. The mineral is thus a member of the linnaeite (Co_3S_4) family.

MILLERITE NiS AT SUDBURY

The presence of millerite in Vermilion ores in close association with violarite was first noted by the authors. Previous observers mistook this mineral for pentlandite. Millerite differs from pentlandite in that it is strongly anisotropic whereas pentlandite is isotropic. Consequently it is not surprising that before the use of the polarizing reflecting microscope became general, the presence of millerite was unsuspected.

Millerite is somewhat harder than violarite and stands up in relief above it. The properties of pentlandite and millerite are compared in tabular form as follows:

PENTLANDITE, (Ni, Fe)S

Color, pale brass yellow; almost identical with pyrite

Isotropic.

Rough cubic cleavage.

No prismatic structure.

Easily scratched by needle.

Etch tests

HNO_3 ...... slowly stains iridescent.
HCl .... negative.
KCN .... "
$FeCl_3$ .... "
KOH .... "
$HgCl_2$ .... "

MILLERITE, NiS

Pale brass yellow; almost identical with pyrite.

Strongly anisotropic.

No cleavage.

Some specimens have prismatic structure; others lack it.

Scratched with difficulty.

Etch tests

HNO_3 ...... slowly stains iridescent.
HCl .... negative.
KCN .... "
$FeCl_3$ .... "
KOH ...... "
$HgCl_2$ ...... Stains brown in places. Some areas negative.

The presence of millerite at Sudbury was noted by Barlow many years ago.[7] The occurrence observed was in the Copper Cliff mine 150 feet below the surface. It was regarded as supergene and a replacement of pentlandite.

Violarite at Julian, California

The nickel ores of the Friday mine, Julian, California, have been studied by F. C. Calkins,[8] Tolman and Rogers,[9] Hudson,[10] and Buddington.[11] The writers had the use of Calkins's original collection, now in the U. S. National Museum.

The deposit lies near the crest of the range between San Diego and the Imperial Valley. The range proper is a northward continuation of the mountain system which forms the backbone of Lower California. This range, which is predominantly granitic in character, is invaded by a stock of gabbro which has an area at the surface of at least one square mile. The ores occur as irregular replacements in this gabbro. Pyrrhotite predominates; chalcopyrite is abundant in places. Tolman and Rogers, also Hudson, report the presence of pentlandite. Calkins, Buddington and the present authors failed to observe that mineral. The nickel mineral is intergrown with pyrrhotite and chalcopyrite in patterns indicating that it is contemporaneous with those minerals. At least there are no textures suggesting replacement as far as the three minerals mentioned are concerned. Later than these three minerals and traversing them in veinlets is a hard pale brass colored mineral. Calkins calls this mineral pyrite but Buddington suggests that it may be marcasite. Inspection in reflected polarized light shows that the mineral is isotropic, hence it is probably pyrite. Still later than pyrite are siderite veinlets (called calcite by previous writers) which traverse the entire section including the pyrite veinlets.

The nickel mineral was called polydymite by Calkins; it has the following properties:—

[7] Barlow, A. E., The Sudbury Mining District. *Geological Survey of Canada, Annual Report,* vol. **14**, Part H, p. 98, 1904.

[8] Calkins, F. C., An occurrence of nickel ore in San Diego County, Calif. *U. S. Geol. Survey, Bull.* **640**, pp. 77–82, 1916.

[9] Tolman, C. F. and Rogers, A. F., A study of the magmatic sulfid ores. *Leland Stanford Jr. Univ., Pub.,* **1916**, pp. 40–41.

[10] Hudson, F. S., Geology of the Cuyamaca region of California. *Pub. Univ. o Calif.,* vol. **13**, 1922.

[11] Buddington, A. F., *Op. cit.,* p. 537.

Hardness, about the same as pyrrhotite.

Color, galena white.

Isotropic.

Perfect cubic cleavage, almost equal to that of galena.

Fairly strong magnetism.

Etch tests.—

HNO$_3$ effervesces; mineral turns dark.

HCl no effect on surface but drop colors yellow or green.

KCN negative.

FeCl$_3$ negative.

KOH negative.

HgCl$_2$ negative.

These properties correspond exactly or very nearly so to those of polydymite from the type locality,–Grunau, Westphalia. The size of the areas of the nickel mineral as shown in polished sections of Friday ores gave a promise of obtaining material sufficiently pure for analysis. Material from 40 polished surfaces was obtained by scratching the surfaces with the needle in the manner already described for Sudbury violarite.

The total amount of material obtained was about 0.12 gm. It was pure except for siderite which crossed the mineral, in minute branching veinlets (see Fig. 4), and a few grains of chalcopyrite. The removal of this siderite was a problem of some difficulty. It is too near the nickel mineral in specific gravity to allow separation by means of heavy liquid. The electromagnet could not be used for this purpose as both siderite and the nickel mineral are magnetic. The method adopted was to dissolve out the siderite by gentle warming in 1:1 HCl. This method involves some risk as some sulphides are measurably soluble in HCl. Inspection of the material after this treatment showed that the sulphide had not been acted on by the acid. The remaining material was placed in a separatory funnel containing heavy solution and the quartz and other insoluble gangue minerals were floated off.

Analysis of the sulphide residue gave the following results, the copper being again calculated as chalcopyrite:

		Ratios	Ratios after calculation of Cu as CuFeS$_2$	
Insoluble	1.31	....	....	
Nickel	33.94	.578	.578	
Cobalt	2.50	.042	.042	
Copper	1.05	.017	....	.949 = 3 × .316
Iron	19.33	.346	.329	
Sulphur	42.17	1.315	1.281	1.281 = 4 × .320

The formula obtained is $(Ni, Fe)_3S_4$.

The results are almost identical with those yielded by the Vermilion material. This mineral is undoubtedly violarite, in spite of its lack of a violet color. The Friday violarite contains more cobalt than the Vermilion ore and this may account for its white color.

POLYDYMITE, Ni_3S_4

Polydymite has been reported by many authors from many localities but in every instance when their description is checked or their material examined in the reflecting microscope, the supposed polydymite has proved to be another mineral, usually violarite. As far as known, genuine polydymite has never been noted in a North American locality and the only place where it is definitely known to occur is the type locality, Grunau, Westphalia.

A specimen from that locality examined microscopically in polished section gave the following properties:

> Color—white with a tinge of yellow.
> Hardness—readily scratched by needle.
> Isotropic.
> Rough cubic cleavage.
> *Etch tests.*
> HNO_3 effervesces slowly; mineral darkens.
> HCl   no effect on mineral; drop turns yellow.
> KCN   negative.
> $FeCl_3$ negative.
> KOH   negative.
> $HgCl_2$ negative.

The analysis after deducting for impurities is S 41.09, Ni 54.30, Co 0.63, Fe 3.98 = 100 (Dana: *System of Mineralogy*).

The formula usually given for the mineral is Ni_4S_5. Wherry and Foshag in reviewing the analysis show that the formula is more probably Ni_3S_4.[12] In view of the very close similarity in physical properties and etch tests of polydymite to violarite, that conclusion is undoubtedly correct.

Polydymite is thus the iron-and-cobalt-free end member of the isomorphous series $(Ni, Co, Fe)_3S_4$. Linnaeite (Co_3S_4) is the

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[12] Wherry, E. T. and Foshag, W. F., The Sulfide Minerals. *Jour. Wash. Acad. of Sciences*, vol. 10, p. 495, 1920.

nickel-and-iron-free and member. The corresponding iron-bearing end member (Fe_3S_4) has not been reported.

SIEGENITE $(Ni,Co)_3S_4$ IN MADISON CO., MO.

The presence of siegenite in southeastern Missouri was known prior to 1857 when an analysis of a sample from Mine la Motte, Madison County, was made by Genth. (See Dana: *System of Mineralogy*). This mineral is usually reported as linnaeite, but in Madison County the percentage of nickel usually exceeds that of cobalt, hence siegenite is a more correct designation.

Siegenite occurs closely associated with chalcopyrite and galena in the disseminated lead ores of the region. It was formerly obtained as a by-product from the concentration of lead ores, but deeper exploration revealed the presence of comparatively rich cobalt-nickel-copper sulphides with lesser amounts of lead. These ores are found at the base of the Bonneterre dolomite (Cambrian) and extend into the underlying Lamotte sandstone (Cambrian). The most extensive deposits are those of the Missouri Cobalt Co, formerly the North American Lead Co., Fredericktown, Mo., and were worked prior to 1920 when the property was closed down.[13]

A specimen of ore from this property was donated to the authors by Mr. C. E. Siebenthal. Examined in polished section, it was found to consist of about equal proportions of sulphides and gangue minerals, the latter being chiefly quartz with a smaller proportion of shale. The sulphides were estimated to consist of approximately 45% chalcopyrite, 45% siegenite and 10% galena. A notable feature is the total absence of pyrite and pyrrhotite from the specimen. The minerals were very fine grained and so intimately admixed that there was no possibility of isolating the siegenite for analysis. However, the accompanying sulphides, chalcopyrite and galena, are easily deducted in a calculation based on an analysis of the whole sample. The sample was crushed to 80 mesh and was passed twice through a separatory funnel containing methylene iodide in order to eliminate as much of the gangue as possible. The resultant product was analyzed by Mr. J. G. Fairchild of the U. S. Geological Survey with the following results:

[13] Buehler, H. A., Biennial report of the State Geologist, *Missouri Bureau of Geology and Mines*, pp. 55–56, 1919,

	Ratios	After deduction of PbS	After deduction of CuFeS$_2$	
Insoluble	11.88	....	....	....
Lead	9.40	.045	....	....
Copper	13.10	.206	.206	....
Iron	15.17	.271	.271	.065 ⎫
Cobalt	8.72	.148	.148	.148 ⎬ .405 = 3 × .135
Nickel	11.27	.192	.192	.192 ⎭
Sulphur	30.57	.953	.908	.496 .496 = 4 × .124

100.11

The formula may be expressed $(Ni,Co,Fe)_3S_4$. This analysis is compared with an earlier analysis as follows:

Siegenite, calculated from above analysis:

Ni	Co	Fe	S	Pb	Insol.	
28.52	22.02	9.21	40.25	....	....	= 100.00

Siegenite, analyzed by F. A. Genth, 1857:

Ni	Co	Fe	S	Pb	Insol.	
30.53	21.34	3.37	41.54	0.39	1.07	= 98.34

Microscopic examination of a polished section of siegenite from the same specimen gave the following results:

Color—cream with a tinge of yellow; indistinguishable from that of linnaeite.
Hardness—harder than chalcopyrite but scratched readily by needle.
Isotropic.
No cleavage pits observed.
Etch tests.—
HNO$_3$ slowly effervesces and stains brown; brings out scratches.
HCl   negative.
KCN   negative.
FeCl$_3$ negative.
KOH   negative.
HgCl$_2$ seems to stain in places; doubtful.

The above properties are very similar to those of both polydymite and linnaeite. They differ from those of violarite from Julian, Cal., which likewise contains cobalt, in the absence of a perfect cubic cleavage and in the yellower color of siegenite.

BRAVOITE $(Ni, Fe)S_2$

Bravoite was first discovered in the vanadium mines at Minaragra, Peru, and was analyzed and described by Hillebrand.[14] The

[14] Hillebrand, W. F., *Amer. Journal of Science*, Ser. 4, vol. **24**, p. 151, 1907.

analysis after the deduction of impurities was as follows:

<div align="center">Ni   18.23,   Fe   29.46,   S   52.31.</div>

From this Hillebrand derived the formula $(Fe, Ni)S_2$ and considered that the mineral was nickeliferous pyrite.

Buddington obtained material collected by D. F. Hewett from the type locality, polished the ore and examined it microscopically. He makes the following observations[15]:

> "The mineral occurs as grains in 'quisqueïte.' With reflected light it has a pallid gray color with a violet hue and shows three well-defined intersecting cleavages. Its hardness is a little less than 5. Etch tests gave the following results: HNO_3—effervesces and turns blue gray; HCl, $HgCl_2$, KCN, KOH and $FeCl_3$—negative. One grain reacted slightly with KOH and rubbed faint brown."

More recently there has been available to American mineralogists, bravoite from Mechernich, Germany, which has been described by Kalb and Meyer.[16] The mineral occurs as individual pyritohedrons, crystal rusts, and massive.   It occupies open spaces between conglomerate beds and small fissures and cavities in in the conglomerate adjacent to the main lead-zinc ore body at Mechernich.   The crystals have a remarkable zonal structure which is especially apparent on polished surfaces.   Zones of a violet-colored mineral alternate with zones of a brass yellow mineral, the boundaries of the zones paralleling the pyritohedral planes. (See Fig. 8). The violet colored zones do not all have the same tinge of violet; a zone of light-violet mineral may lie adjacent to a zone of deep-violet mineral, or a zone of deep-violet mineral may be separated from a zone of light violet mineral by one of the brass-yellow mineral. Material from one of the violet-colored zones and from one of the brass-yellow zones were analyzed separately by the authors cited, with the following results:

	Ni	Co	Fe	Cu	S	Insol.
Violet-colored zone	24.73	3.28	17.08	0.47	51.15	0.40
Yellow-colored zone	4.40	tr.	38.02	2.80	50.77	2.50

The formula for both zones can be expressed as $(Ni, Fe)S_2$. The above authors state that the violet-colored zone can be termed "bravoite" and the yellow zone "nickeliferous pyrite." The different shades of violet, are probably due to different proportions of

[15] *Op. cit.*, p. 526.

[16] Kalb, G. and Meyer, Emil, Die Nickel-und Kobaltführung der Knottenerz-lagerstätte von Mechernich. *Centralbl. f. Mineral., Abt. A.*, p. 26, 1926.

nickel and iron.[17] The present authors obtained a specimen of Mechernich bravoite through the kindness of Dr. Buddington. Examined microscopically in reflected light it gave the following properties:

Color—violet gray.
Hardness—cannot be scratched by needle (greater than 5.5).
Isotropic.
No indication of cleavage.
Etch tests.—
HNO_3. Fumes tarnish; mineral stains iridescent and brings out zonal structure.
HCl, KCN, $FeCl_3$, KOH, $HgCl_2$—negative.

These properties are very different from those of the mineral from Minaragra as reported by Buddington. The Mechernich mineral occurs in well-formed crystals up to one centimeter in diameter and unmixed with other minerals. The Minaragra mineral was not examined under the reflecting microscope by Hillebrand before analysis and the present writers are inclined to question this analysis. On the other hand the properties of the Minaragra mineral as reported by Buddington check exactly with those of violarite. The cubic cleavage and hardness are especially significant. The present authors were unable to secure a satisfactory specimen of the Minaragra nickel mineral.

Nickel Mineral X.

The designation nickel mineral X was given by Buddington to a violet-colored nickel-iron sulphide which replaces pentlandite in veinlets following cleavage cracks, grain boundaries and other open spaces. No grains with crystal faces were observed. The properties as determined by Buddington and checked by the authors are as follows:

Color—violet grey.
Hardness—medium.
Cleavage—cubic.
Etch tests.—
HNO_3—effervesces slowly; mineral darkens.
HCl—no effect on mineral; drop turns yellow.
KCN, $FeCl_3$, KOH, $HgCl_2$—negative.

[17] The violet tinge of bravoite was not specifically mentioned by Kalb and Meyer. They describe its color as steel-gray. It is not apparent from their description whether or not they examined the mineral in polished section, but the illustration accompanying the article seems to indicate it.

Buddington's work was done before the use of polarized reflected light became general. Observations with polarized light on polished sections from his collection were made by the authors. In specimens from some localities nickel mineral X is isotropic; from other localities it is weakly anisotropic.

ISOTROPIC	ANISOTROPIC
Gap, Pa.	Dracut, Mass.
Tasmania claim, Alaska.	Pigeon Point, Minn.
Admiralty, Alaska.	Bohemia mine, Alaska.
Emory Creek, B. C.	Floyd Co., Va.

The violet color is best seen where nickel mineral X is in contact with pentlandite. Where the replacement is nearly or entirely complete as in the Tasmania, Admiralty and Gap specimens, nickel mineral X is in contact with pyrrhotite, and here its violet color is somewhat obscured by that of pyrrhotite. The color of nickel mineral X seems to be ashy-gray in these specimens. Where the replacement is nearly complete, as in the localities mentioned, the mineral is very crumbly and tends to break down chemically when exposed to the atmosphere. This is in contrast to Sudbury violarite which is stable for long periods and led Buddington to believe that the two minerals are not identical. However, in specimens where the replacement is not far advanced, such as the Dracut, Emory Creek, Pigeon Point and Floyd County specimens, nickel mineral X shows no signs of being crumbly or breaking down chemically.

The ore deposits where nickle mineral X occurs have nearly all been well described by Buddington and by Lindgren and Davy. These descriptions will not be repeated here. Two additional localities, Emory Creek, B. C., and Floyd County, Va., have also been described by others and are summarized here for convenience.

EMORY CREEK, B. C. The nickel prospect on Emory Creek, British Columbia, is well described by Cairnes.[18] The prevailing rocks are batholithic and have the average composition of a quartz diorite. Invading these rocks is a dike of fresh hornblendite of unknown dimensions. The country is precipitous and exploration is difficult. The ore body is a mass of nearly solid sulphide 75 feet across and outcropping as a cliff 30 feet high. Exploration had not

[18] Cairnes, C. E., Nickeliferous Mineral Deposit, Emory Creek, Yale Mining Division, B. C. *Geological Survey of Canada, Summary Report*, **1924**, Part A, pp. 100–105.

revealed the size of the ore body at the time of Cairnes's visit. Included in the sulphide mass and in its vicinity is considerable hypersthene which appears to be of primary origin. Feldspar is absent or only sparingly present. The predominant sulphide is pyrrhotite; chalcopyrite and pyrrhotite are subordinate. Cutting pentlandite are veinlets of a mineral with nearly the color of pyrrhotite. These veinlets are confined to the pentlandite and follow cracks in it. Cairnes suspected that this mineral is identical with nickel mineral X but did not have specimens from other localities with which to make comparisons. A specimen from Emory Creek was kindly sent by Dr. Cairnes to the authors which enabled them to identify the unknown mineral in this specimen as nickel mineral X. Cairnes states that much oxidation is in evidence where the specimen was obtained. It will be interesting to find out whether or not the mineral persists in depth.

FLOYD COUNTY, VIRGINIA. Near the north border of Floyd County Virginia, is a small nickel prospect not of commercial importance. It is located near the junction of Flat Run and Lick Fork, two head water streams of the South Fork of Roanoke River. The deposit has been described by Watson[19] and by Ross.[20] Specimens of sulphide ore collected by Dr. Ross were made available to the authors for study.

According to Ross, the prevailing rocks of the region are schists and gneisses of pre-Cambrian age. Cutting these older rocks is a compound dike consisting of three distinct kinds of rocks, a dark gray fresh rock composed almost exclusively of andesine, a diabase, and a rock which varies in composition between gabbro and pyroxenite. The pyrrhotite vein is a mineralized zone in this compound dike. There are sharp boundaries between diabase, gabbro-pyroxenite and andesinite, but no sharp wall between andesinite and the inclosing wall rock was observed.

The principal sulphide mineral is pyrrhotite. Chalcopyrite and pentlandite are subordinate and sphalerite is present in places as minute inclusions in pyrrhotite. The above ore minerals are complexly intergrown and seem to be contemporaneous. Pyroxene is the principal gangue mineral in the ore specimens. The sulphides

[19] Watson, Thos. L., The occurrence of nickel in Virginia. *Trans. Amer. Inst. Min. Engrs.*, pp. 829–843, **1907,**

[20] Ross, Clarence S., Copper mines of the Southern Appalachians. *U. S. Geol Survey, Unpublished Manuscript.*

are later than pyroxene and traverse it as small branching veinlets which in part follow cleavage planes in the pyroxene. Nickel mineral X cuts pentlandite in tiny veinlets following open spaces. In properties it is identical with the mineral in the localities already cited.

CONCLUSION. Nickel mineral X and violarite are identical in color, hardness, cleavage, polarization and etch tests. Both minerals consist primarily of nickel iron and sulphur. We are therefore convinced that the two minerals are identical.

A major problem left unsolved by us is the relationship between violarite and pentlandite at Sudbury. It is known that these two minerals occur in the same mine but they have not been observed in the same hand specimen. It is hoped that this paper will induce others to undertake the solution of this problem.

SUMMARY

Violarite from Sudbury and the unknown nickel mineral from the Friday mine, Julian, California, were both analyzed and found to be identical. The chemical formula determined is $(Ni, Fe)_3S_4$; the mineral belongs in the isometric system and is closely similar in physical and chemical properties to linnaeite, Co_3S_4 and polydymite, Ni_3S_4. The authors believe that violarite from these two localities is hypogene. Nickel mineral X and violarite have the same physical properties and contain the same elements, hence are believed to be identical.

Fig. 1. Violarite (supergene) replacing pentlandite in veinlets which follow cleavage cracks and other open spaces. Violarite veinlets do not extend into surrounding pyrrhotite. Dracut, Mass., nickel mine. ×83.

Fig. 2. Violarite (supergene) replacing pentlandite. A more advanced stage of replacement than shown by Fig. 1. Pigeon Point, Minn. ×200.

Fig. 3. Violarite (supergene) replacing pentlandite. A still more advanced stage of replacement. Only a few small remnants of pentlandite have survived attack. Gap, Pa., ×300.

Fig. 4. Violarite (hypogene) surrounded by chalcopyrite and pyrrhotite. The violarite boundaries are straight. Violarite here shows tendency to form crystal planes. Veinlets of siderite follow cleavage cracks and fill triangular cleavage pits in violarite. Perfect cubic cleavage of violarite clearly shown in lower part of picture. Friday mine, Julian, Cal. ×38.

Vl   violarite, $(Ni, Fe)_3S_4$
Pn   pentlandite, $(Ni, Fe)S$
Po   pyrrhotite, $FeS+S$
S   siderite, $FeCO_3$
Cp   chalcopyrite
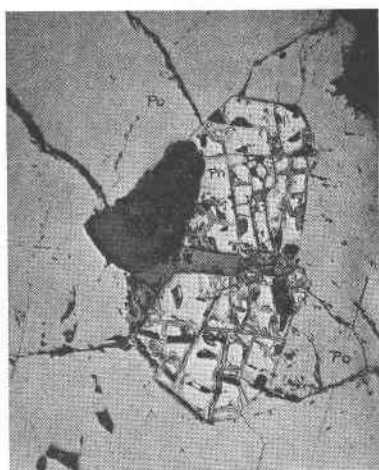
Fig. 1.

Fig. 2.

Fig. 3.
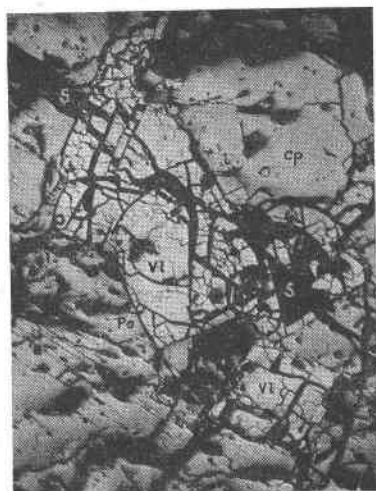
Fig. 4.

FIG. 5. Millerite (probably supergene) halos surrounding violarite (hypogene). Boundaries between millerite and chalcopyrite are sharp. Where millerite is absent, boundaries between violarite and chalcopyrite are sharp. Boundaries between millerite and violarite are fuzzy. Violarite "nodules" are composed of aggregates of small grains of diverse orientation. This is better shown in Fig. 7. Vermilion mine, Sudbury, Ont. ×38.

FIG. 6. Chalcopyrite veinlets crossing violarite. Chalcopyrite is apparently later than violarite. There is a possibility however that violarite completely replaces some pre-existing mineral which was earlier than chalcopyrite; if this were true, violarite could be later than chalcopyrite. Violarite areas are rimmed by millerite. Vermilion mine, Sudbury, Ont. ×38.

FIG. 7. Millerite replacing violarite. A more advanced stage than that shown in Fig. 5. Vermilion mine, Sudbury, Ont. ×60.

FIG. 8. Concentric shells of bravoite and nickeliferous pyrite. In the bravoite areas different shades of violet paralleling the pyrite bands are clearly seen. The pyrite areas parallel pyritohedral crystal faces. Mechernich, Germany. ×246.

Ml   millerite NiS
Vl   violarite (Ni, Fe)$_3$S$_4$
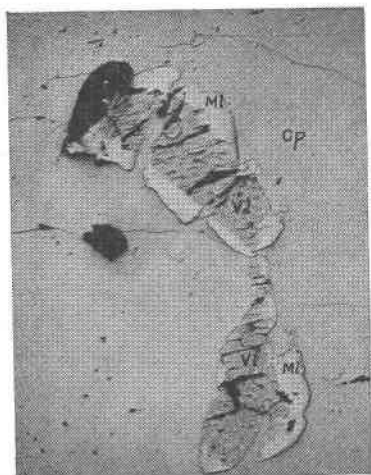Cp   chalcopyrite, CuFeS$_2$
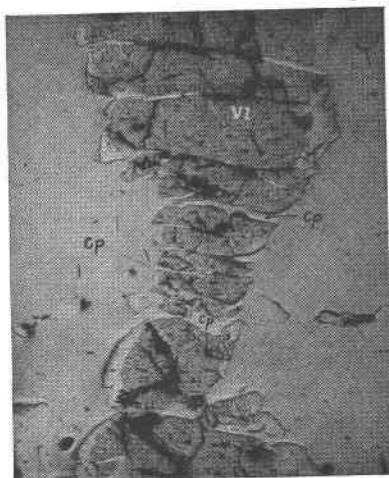Br   bravoite (Ni, Fe)S$_2$
Py   pyrite (nickeliferous), (Fe, Ni)S$_2$
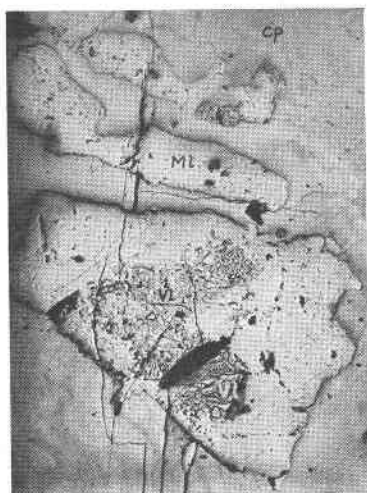
FIG. 5.

FIG. 6.

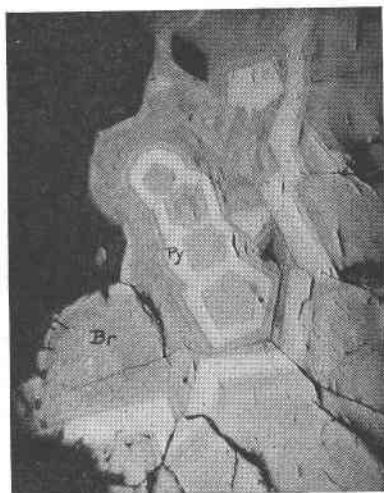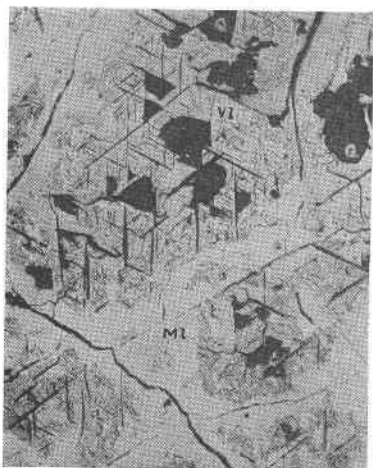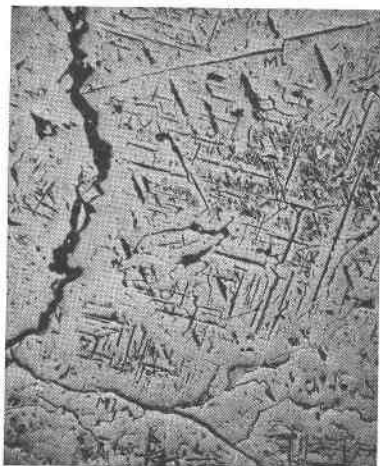FIG. 7

FIG. 8.

FIG. 9.   FIG. 10.

FIG. 9. Violarite showing perfect cubic cleavage. Quartz crystals are replacing violarite, the quartz boundaries in part aligned along cleavage faces of violarite. Some of the cleavage cracks of violarite extend into the quartz areas, showing that quartz has inherited cleavage of violarite. Millerite is replacing violarite, the replacement following irregular cracks. Levack mine, Sudbury, Ont. ×60.

FIG. 10. Violarite showing perfect cleavage being replaced by millerite. Levack mine, Sudbury, Ont. ×20.

Vl   violarite
Ml   millerite
Q   quartz