

## Cobalt- and Iron-Rich Violarites from Virginia

JAMES R. CRAIG, AND JOHN B. HIGGINS

*Department of Geological Sciences,  
Virginia Polytechnic Institute and State University,  
Blacksburg, Virginia 24061*

### Abstract

Iron- and cobalt-rich violarites—containing up to 43 and 9.7 weight percent of the elements respectively—occur as secondary minerals in the ores of the Lick Fork deposit, Floyd County, Virginia. The ores, which are associated with a mafic dike, initially consisted of hexagonal pyrrhotite and pentlandite, but now also contain abundant monoclinic pyrrhotite and minor pyrite as well as violarite. Metal to sulfur ratios of the violarites range from 3.03:4.00 to 3.31:4.00.

### Introduction

Violarite, the iron-nickel member ( $\text{FeNi}_2\text{S}_4$ ) of the thiospinel (or linnaeite) series of minerals, occurs in the ores of the Lick Fork deposit (also known at times as the Mackusick, Flat Run, and John Light's mine) in northeastern Floyd County, Virginia ( $37^\circ 05'$  N., Lat.;  $80^\circ 12' 30''$  W. long.) (Fig. 1). This occurrence of violarite is of interest because it represents one of the few occurrences of nickel in the southern Appalachians and because it contains cobalt-rich and iron-rich violarites.

The deposit was first worked before the Civil War and has been prospected intermittently for the past 70 years, but has never been mined on a commercial basis. The history of abortive mining ventures at Lick Fork has been summarized by Dietrich (1959) and Luttrell (1966).

### Geologic Setting

The Lick Fork deposit is situated in the complex of "undifferentiated" metamorphic rocks of the western edge of the Blue Ridge of southwestern Virginia. Watson (1907a, b) referred to the deposit as a "vein" associated with an igneous dike ranging in composition from a pyroxene syenite to a basic gabbro. He described the ores in the following manner: "The sulfides are distributed through the rock in small irregular areas both connected and disconnected, and in stringers and veinlets, which penetrate the rock in all directions. These

irregular, small areas of ore may be composed entirely of sulfides or the sulfides may enclose minute areas of the rock minerals."

Ross (1935) reexamined the ores and reported the occurrence of grains of pentlandite with violarite rims; his descriptions were repeated by Dietrich (1959). The host gneisses and the gabbroic rocks associated with the ores bear a tectonic metamorphic overprint in the form of undulatory extinctions and bent twin lamellae.

### Ore Mineralogy

The Lick Fork ores consist predominantly of pyrrhotite with lesser amounts of chalcopyrite, violarite, pentlandite, and pyrite (Figs. 2, 3). The pyrrhotite occurs as irregularly disseminated grains grading into thin (1 mm) stringers and veinlets, and is primarily hexagonal; however, monoclinic pyrrhotite is common along fractures and along most grain boundaries as rims and irregular, flame-like structures (Fig. 2). Pentlandite is present as a few scattered remnants in some violarite grains (Fig. 3). Chalcopyrite occurs as rare disseminated grains in pyrrhotite. Pyrite is extremely rare and is present only as a few, apparently late-formed crusts and veinlets with iron oxides and hydroxides in fractures in the pyrrhotite.

Violarite is dispersed throughout the mineralized zone as anhedral-to-rounded grains and as irregular veinlets up to 0.1 mm across. Some parting in the violarite appears to be pseudomorphous after the

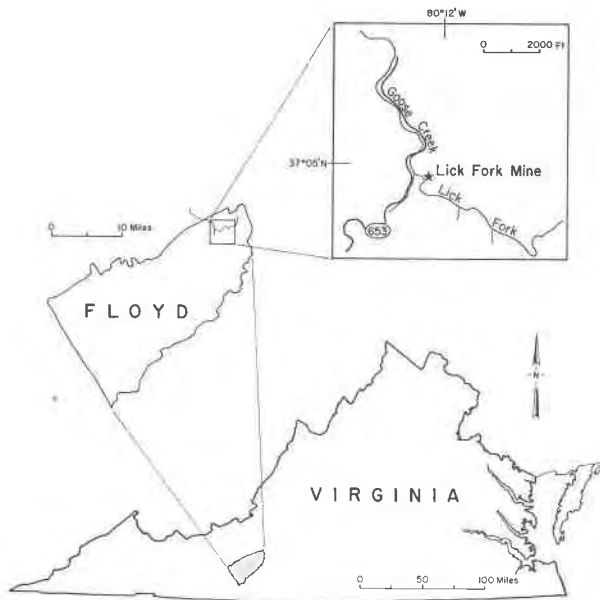


FIG. 1. Location map of the Lick Fork deposit.

(111) cleavage in pentlandite but it cannot be traced from one mineral to the other where they are in contact. The violarite is only occasionally in contact with hexagonal pyrrhotite; generally a 0.01 to 0.1 mm thick rim of monoclinic pyrrhotite intervenes.

The violarite and the accompanying minerals were analyzed on an ARL-EMX microprobe at 15 kV and 0.15  $\mu$  amp beam current using synthetic  $\text{Co}_3\text{S}_4$ , NiS, FeS, and CuS as standards; data reduction was accomplished by the EMPADR VII program (Rucklidge and Gasparrini, 1969). The analyses of the various phases are given in Table 1.

The violarites of this deposit range widely in composition from ~24 percent Fe, 24-30 percent Ni, and 3.9-9.7 percent Co to ~43 percent Fe, 13 percent Ni, and 0.2-1.4 percent Co (see Table 1 and Fig. 4). Copper contents are negligible. The metal-to-sulfur ratios, like those of violarites from other deposits, are metal-rich ( $M_{3.03}\text{S}_4$  to  $M_{3.31}\text{S}_4$ ) relative to the ideal  $M_3\text{S}_4$  composition. There is not, however, any discernible correlation of metal-to-sulfur ratio with variation in Fe-to-Ni ratio. Confirmation of the violarite structure was not feasible by X-ray powder diffraction because of the small size of the grains, but one typical grain was chipped out of a polished section and examined by means of a Gandolfi camera. Although the lines were diffuse, the structure was clearly that of a thiospinel

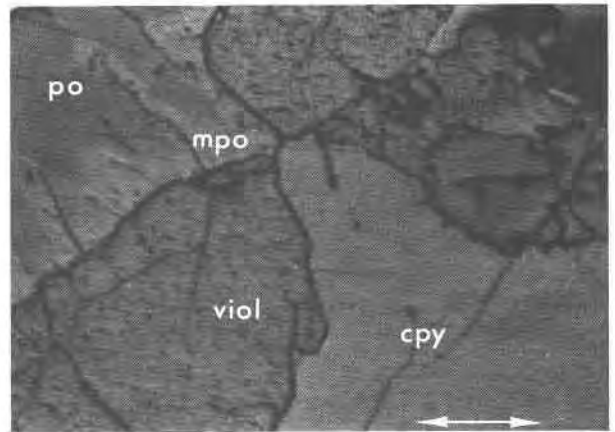


FIG. 2. Typical Lick Fork violarite (viol) with associated hexagonal pyrrhotite (po), monoclinic pyrrhotite (mpo), and chalcopyrite (cpy). The arrow is approximately 20 microns in length.

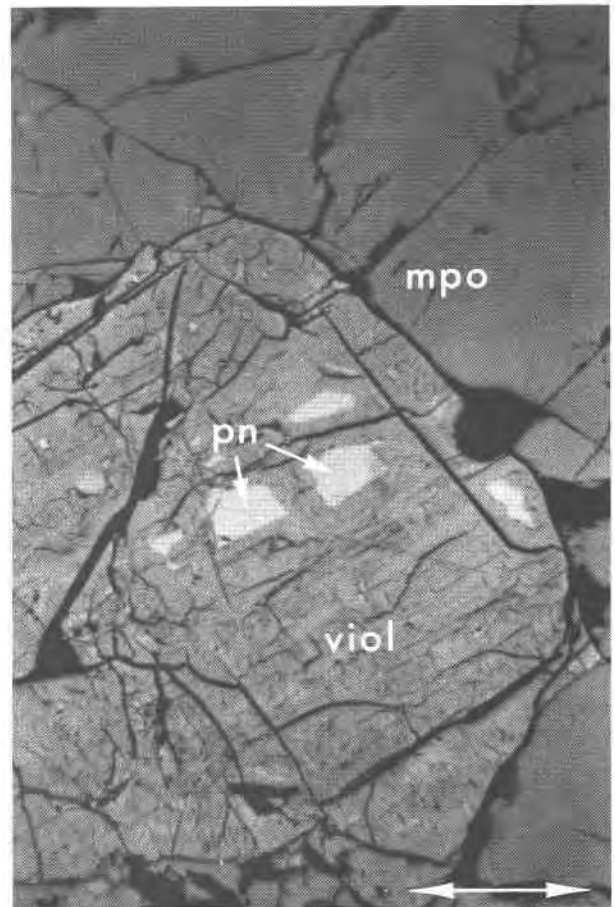


FIG. 3. Grain of violarite (viol) with remnant pentlandite cores (pn) in monoclinic pyrrhotite (mpo). The arrow is approximately 10 microns in length.

with a unit cell dimension of approximately 9.46 Å, close to that of stoichiometric  $\text{FeNi}_2\text{S}_4$  (Craig, 1971). The varieties of violarite found are indistinguishable in reflected light, all being light violet brown and isotropic. Triangular cleavage patterns, probably pseudomorphous after pentlandite, are visible in some violarite grains. On the basis of microprobe scans, the more nickel-rich compositions are much more abundant than the iron-rich ones. The individual grains are homogeneous, showing no variation in Fe, Ni, Co, or S contents from center to edge.

The Lick Fork violarites, as those from many deposits, exhibit iron contents (7 to 25 percent) which are far in excess of stoichiometric  $\text{FeNi}_2\text{S}_4$ . The most iron-rich of the violarites actually more closely approach greigite composition ( $\text{Fe}_3\text{S}_4$ ) than nominal violarite composition. These violarites are similar in Fe/Ni ratio to the type 2 reported by Misra and Fleet (1974) in the Werner Lake "A" ore body but are considerably more iron-rich (see Fig. 4) than those reported by Desborough and Czamanske (1973) from Kimberlite nodules. Their metal-to-sulfur ratio, however, is 3.15 to 4.00, which lies between the 3.01 to 4.00 value for the Werner Lake "A" specimen and Desborough and Czamanske's 3.27 to 4.00 value.

### Origin of the Violarite

Neither the origin of the Lick Fork deposit nor of the violarite in it is unequivocal. The general texture of the sulfides in the silicate matrix is quite similar to that in disseminated ores in larger nickel deposits such as those at Sudbury, Ontario. It is thus likely that the sulfides are intimately related to the gabbroic rocks, and possibly formed from an immiscible sulfide melt. The feldspars, pyroxenes, and micas are generally fresh and do not show any post-magmatic, hydrothermal alteration effects. Most silicate alteration is confined to narrow bleached rims on pyroxenes in the mineralized zone.

On the basis of the known phase relations of the Fe-Ni-sulfides (Misra and Fleet, 1974; Craig, 1973), the sulfide mineral assemblages at Lick Fork appear to represent supergene or low temperature hydrothermal adjustments. The spatial relationships of pentlandite and violarite, and the similarity of their cobalt contents—violarite (Table 1, analysis #6) contained 3.33 wt percent Co compared to 3.11 for coexisting pentlandite (analysis #9)—appear to indicate that much of the violarite formed as an alteration product of the pentlandite. This is

TABLE 1. Microprobe Analyses of Ore Minerals from Lick Fork

Mineral	Element (weight percent)					Sum	"x" in $\text{M}_x\text{S}_4$
	Fe	Ni	Co	Cu	S		
Violarite							
1	24.3	28.5	3.85	0.17	41.9	98.7	3.03
2	22.9	28.6	5.34	0.00	41.9	98.7	3.03
3	24.0	30.7	5.82	0.38	41.0	101.9	3.31
4	24.1	24.3	9.69	0.10	42.4	100.6	3.06
5	24.2	29.4	4.33	0.03	43.1	101.0	3.15
6	32.5	22.5	3.33	0.00	42.0	100.3	3.12
7	43.1	13.1	0.19	0.00	40.7	97.1	3.15
8	43.1	12.7	1.35	0.00	41.3	98.4	3.14
Pentlandite							
9	34.8	31.1	3.11	0.00	33.7	102.6	--
Pyrrhotite							
10	61.1	0.02	0.10	0.00	40.9	102.1	--
11	56.6	0.37	0.13	0.00	43.3	100.3	--
12	56.8	0.00	4.23	0.00	39.3	100.3	--
Chalcopyrite							
13	31.9	0.01	0.17	35.00	33.9	101.0	--
Pyrite							
14	47.4	0.40	0.09	0.13	50.4	98.4	--

certainly compatible with Misra and Fleet's (1974) observed correlations of cobalt contents of coexisting pentlandites and violarites. The rather wide variation in Fe/Ni ratios of the violarites appears to indicate that some may have formed in a somewhat different manner. The more iron-rich violarites thus may well represent replacement of pyrrhotite, which is generally low in both nickel and cobalt. The low cobalt and nickel contents of the pyrite (analysis #15) suggest that it did not form with the high cobalt violarite but rather with the low cobalt violarite or later.

If pyrite and pentlandite constitute a stable low temperature assemblage as suggested by Kullerud, Yund, and Moh (1969), Misra and Fleet (1974) and Craig (1973), then the pyrrhotite-violarite assemblages at Lick Fork must be metastable. However, the increasingly frequent reports of occurrences of pyrrhotite-violarite assemblages (Kambalda, Australia—Nickel, 1973; Gap Mine, Pennsylvania—Speer and Martin, 1974; Whistle and Discovery Site, Sudbury—Arnold and Malik, 1974) suggest that the assemblage is persistent and perhaps even stable under some conditions. The compositions of all Lick Fork violarites are far more iron-rich (7 to 25 percent) than stoichiometric  $\text{FeNi}_2\text{S}_4$  and thus may represent only metastable phases. Nickel (1973) has noted that metastable secondary violarite compositions are more a function of the mineral replaced than equilibrium relationships. On the other hand, experimental work in progress suggests that the presence of cobalt extends the solid solubility limits of iron in violarite.

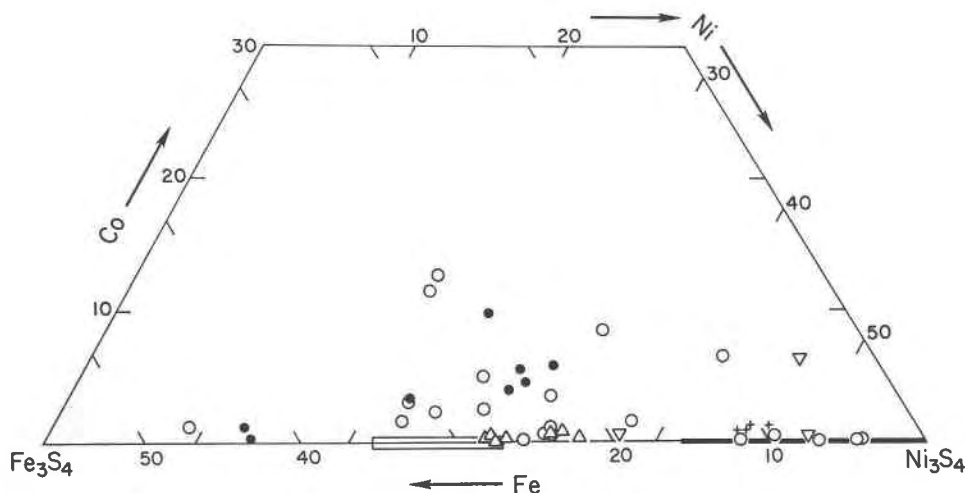


FIG. 4. Compositional range of natural violarites plotted in terms of weight percent iron, nickel and cobalt as projected onto the  $\text{Fe}_3\text{S}_4$ - $\text{Ni}_3\text{S}_4$ - $\text{Co}_3\text{S}_4$  plane. Data are: dots—Lick Fork deposit; crosses—Graterol and Naldrett (1971); triangles—Nickel, *et al* (1974); long box—range of Desborough and Czamanske (1973); circle—Misra and Fleet (1974); inverted triangle—Buchan and Blowes (1968).

### Acknowledgments

We are indebted to Drs. L. J. Cabri, A. H. Clark, and E. H. Nickel for their criticisms of this manuscript during its preparation.

### References

- ARNOLD, R. G., AND O. P. MALIK (1974) Violarite in some nickel ores from Lynn Lake and Thompson Manitoba, and Sudbury, Ontario, Canada. *Can. Mineral.* **12**, 320-326.
- BUCHAN, R., AND J. H. BLOWES (1968) Geology and mineralogy of a millerite nickel ore deposit. *Can. Inst. Min. Metallurgy Bull.* **61**, 529-534.
- CRAIG, J. R. (1971) Violarite stability relations. *Am. Mineral.* **56**, 1303-1311.
- (1973) Pyrite-pentlandite and other low temperature assemblages in the Fe-Ni-S system. *Am. J. Sci.* **273A**, 496-510.
- DESBOROUGH, G. A., AND G. K. CZAMANSKE (1973) Sulfides in eclogite nodules from a Kimberlite pipe, South Africa, with comments on violarite stoichiometry. *Am. Mineral.* **58**, 195-202.
- DIETRICH, R. V. (1959) Geology and mineral resources of Floyd County of the Blue Ridge Upland, Southwestern Virginia. *Bull. Va. Polytech. Inst., Va. Eng. Exp. Ser. No. 134*, 160.
- GRATEROL, M., AND A. J. NALDRETT (1971) Mineralogy of the Marbridge No. 3 and No. 4 nickel-iron sulfide deposits. *Econ. Geol.* **66**, 886-900.
- KULLERUD, G., R. A. YUND, AND G. H. MOH (1969) Phase relations in the Cu-Ni-S and Fe-Ni-S systems. In H. B. D. Wilson, Ed., *Magmatic Ore Deposits. Econ. Geol. Monogr.* **4**, 323-343.
- LUTTRELL, G. W. (1966) Base- and precious-metal and related ore deposits of Virginia. *Va. Div. Mineral Resour. Rep.* **7**, 167.
- MISRA, K. C., AND M. E. FLEET (1974) Chemical composition and stability of violarite. *Econ. Geol.* **69**, 391-403.
- NICKEL, E. H. (1973) Violarite—a key mineral in the supergene alteration of nickel sulphide ores. *Aust. I.M.M. Conf., West. Aust. May 1973*, 111-116.
- , J. R. ROSS, AND M. R. THORNER (1974) The supergene alteration of pyrrhotite-pentlandite ore at Kambalda, Western Australia. *Econ. Geol.* **69**, 93-107.
- ROSS, C. S. (1935) Origin of copper deposits of the Ducktown type in the Southern Appalachian Region. *U. S. Geol. Surv. Prof. Pap.* **179**, 165.
- RUCKLIDGE, J., AND E. L. GASPARRINI (1969) Specifications of a computer program for processing electron microprobe analytical data: *Univ. Toronto Dep. Geol.* **37**.
- SPEER, J. A., AND E. C. MARTIN (1974) Pennsylvania minerals. I. Violarite from the Gap Mine. *Mineral Rec.* **5**, 209-210.
- WATSON, T. L. (1907a) *Mineral Resources in Virginia*. J. P. Bell and Co. Lynchburg, Va., 618.
- (1907b) The occurrence of nickel in Virginia. *Am. Inst. Min. Eng. Bull.* **17**, 829-843.

Manuscript received, July 18, 1974; accepted for publication, October 15, 1974.