

# Manganese Contents of Some Sedimentary Rocks of Paleozoic Age in Virginia

By ERIC R. FORCE and LESLIE J. COX

- A. Manganese Contents of Some Lower Paleozoic Carbonate Rocks of Virginia,  
by Eric R. Force
- B. Manganese Contents of Some Rocks of Silurian and Devonian Ages in Northwest  
Virginia, by Leslie J. Cox

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Chapter A

# Manganese Contents of Some Lower Paleozoic Carbonate Rocks of Virginia

By ERIC R. FORCE

Manganese in Shady Dolomite and Knox  
Group rocks that underlie supergene  
manganese deposits

U.S. GEOLOGICAL SURVEY BULLETIN 1916

MANGANESE CONTENTS OF SOME SEDIMENTARY ROCKS OF PALEOZOIC AGE  
IN VIRGINIA



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## CHAPTER A

# Manganese Contents of Some Lower Paleozoic Carbonate Rocks of Virginia

By Eric R. Force

### Abstract

The lower Paleozoic carbonate formations of Virginia have an apparent potential for shallow-marine sedimentary manganese deposits. Where those formations form the substrate of supergene manganese deposits, they were analyzed for manganese and other elements in this reconnaissance investigation. The highest primary manganese content encountered, in laminar limestones at the base of the Shady Dolomite, was only 0.3 percent. The great disparity in manganese contents of bedrock and overlying supergene deposits is not matched by similar disparities for other insoluble elements, suggesting that supergene enrichment was not simply a result of residual enrichment. Probably manganese in solution, derived from a number of sources, was geochemically trapped in the overburden above certain reactive units. Within this overburden, manganese was further concentrated in the small, high-grade bodies that were mined.

### INTRODUCTION

In recent years, world manganese production has increasingly come from large sedimentary deposits of shallow-marine origin. Stratigraphic units containing valuable manganese concentrations consist of carbonates or fine clastics and represent deposition during high sea level stands, particularly on the margins of stratified (black shale) basins (reviewed by Force and Cannon, 1988). Some of these shallow-marine manganese concentrations are quite inconspicuous.

Virginia is not known to have shallow-marine manganese deposits, but supergene manganese deposits (i.e., manganese concentrations in weathered rock) are present over carbonate units of Early Cambrian, Late Cambrian to Early Ordovician, and Middle Devonian ages. The deposits

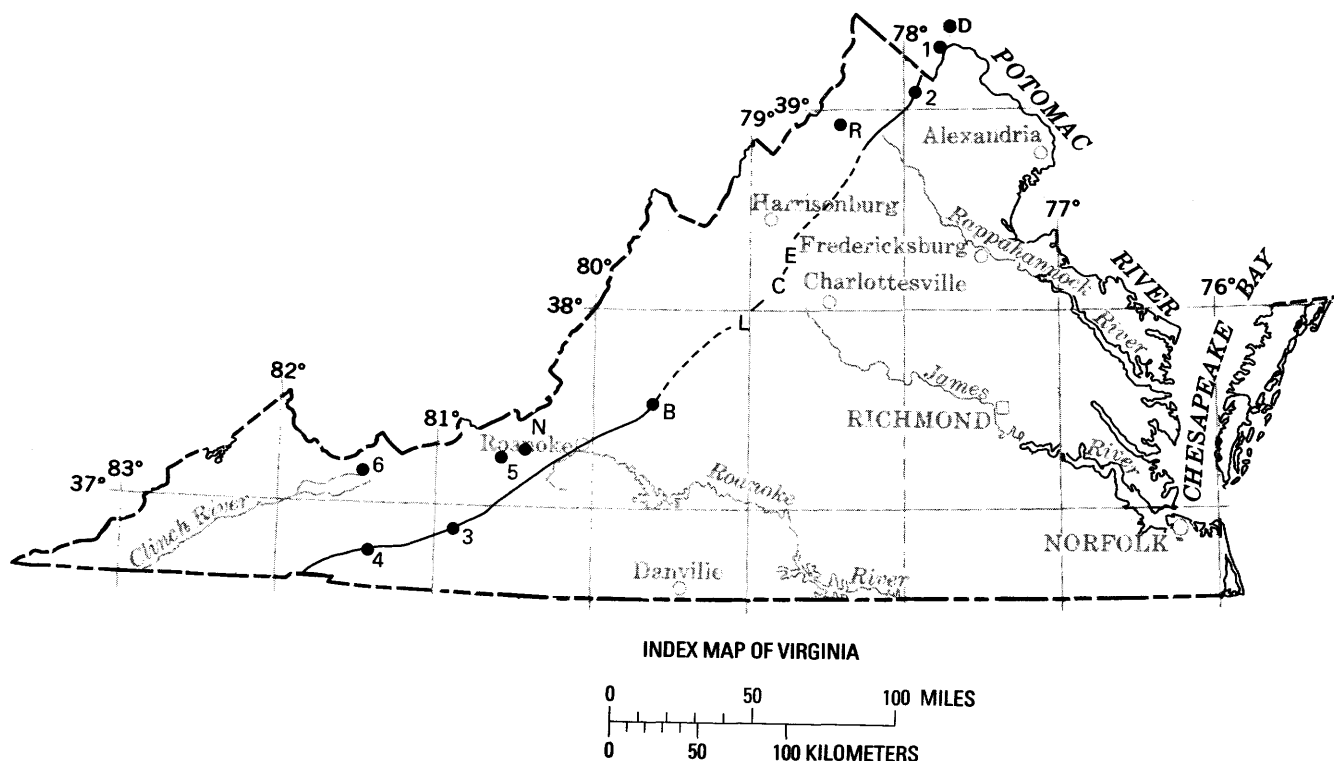
over lower Paleozoic rocks that are discussed in this paper have had the greatest production. None of the supergene deposits are presently mined.

The distribution of supergene manganese concentrations may be a clue to the distribution of manganese in underlying parent rocks. The two lower Paleozoic rock assemblages now represented by supergene manganese deposits in Virginia seem broadly permissive of manganese concentration. They represent deposition in shallow-marine (and slope; Pfeil and Read, 1980) environments. Whether deposition was on the margins of stratified basins is not known in Virginia, but stratified-basin deposits of these ages are known elsewhere (Leggett, 1980; Goodfellow, 1987). The carbonate (mostly dolomitic) units suggest high sea level stands and resulting absence of coarse-clastic dilution, in comparison to adjacent units. Thus the combination of permissive environment and supergene manganese deposits suggests that the manganese contents of these units should be established. Such a reconnaissance investigation is the purpose of this article.

### SUPERGENE DEPOSITS

As recently as World War II, Virginia produced a large share of domestically mined manganese. This manganese came from supergene deposits, mostly over the Lower Cambrian Shady (Tomstown) Dolomite and adjacent rocks (fig. 1). Some production was from supergene deposits over Cambrian-Ordovician Knox Group dolomites and over Devonian rocks. The deposits over Devonian rocks are described separately.

The supergene deposits over lower Paleozoic rocks are described in a voluminous literature from the era of active mining. Hewitt (1916), Hewitt and others (1918), Stose and others (1919), Stose (1942), King (1943, 1950), Knechtel (1943), Stead and Stose (1943), and Miller (1944)



**Figure 1.** Index map showing locations of areas of sample collection, former manganese mining districts, and the outcrop belt of Shady Dolomite. Line is approximate belt of Shady Dolomite, dashed in interval lacking outcrop of lower Shady. The Knox Group, too complex to be shown at this scale, is approximately parallel to and northwest of the Shady.

Sites of sample collection along measured sections:

**Shady Dolomite**

- 1, Harpers Ferry area
- 2, Shenandoah River
- 3, Austinville area
- 4, Marion area

**Knox Group**

- 5, New River
- 6, Tazewell area

Other sites of sample collection:

**Shady Dolomite**

- D, Dargan (Md.)
- B, Buchanan

**Knox Group**

- R, Round Hill

**Former mining districts**

**Shady Dolomite**

- D, Dargan (Md.)
- E, Elkton
- C, Crimora
- L, Lyndhurst-Vesuvius
- 3, Lick Mountain
- 4, Glade Mountain

**Knox Group**

- N, Newport
- 6, Tazewell

are some of the more important descriptions of deposits associated with Shady Dolomite; Stose and others (1919) is the most comprehensive. Stose and Miser (1922) describe the deposits on the Knox Group.

Manganese oxide minerals described from these deposits include pyrolusite, "psilomelane," manganite, and "wad." Sixteen analyses of concentrates listed for deposits associated with Shady Dolomite, apparently representative of the major producers, average 39.9 percent manganese and 7.8 percent iron. For the seven analyses that list alumina, the average is 3.0 percent. The one analysis of a concentrate from a deposit over the Knox Group is similar.

The ores, up to tens of meters thick, are of several types, including (in probable order of importance) (1) concretions and impregnations (locally forming ledges) of manganese oxides in saprolitic clay, (2) solution-collapse or other breccias with manganese-oxide cement, and (3) manganese-oxide detritus in colluvium. All the types are thus heterogeneous material, consisting of high-grade hard minerals in a voluminous barren host that may or may not be soft. Bulk manganese grades are therefore low, except for small tonnages of material.

Theories that have been put forward to explain manganese enrichment in these deposits include:

1. Manganese, present as a minor constituent of underlying carbonate precursors, was residually concentrated in place as insoluble residue by dissolution during weathering (Stose and others, 1919; King and others, 1944; Stose, 1942; Knechtel, 1943; Miller, 1944; Stose and Stose, 1957).
2. Manganese, from either underlying or adjacent formations, became fixed in the high-pH environment of weathering carbonate rock (Hack, 1965). Manganese may have been transported in regional ground waters to the carbonate trap from formations weathering upslope.
3. Manganese may have been transported from depth to a surficial environment of precipitation via local plumbing systems, especially faults (Stead and Stose, 1943; Cooper, 1944).

All these mechanisms appear plausible, and each seems capable of assuming a major share of supply in certain local conditions but seems not to work in others. The trapping of manganese dissolved in ground water is likely where carbonate hosts intercept a ground-water gradient. Hack (1965) has shown that where this condition is not met, few deposits occur in the Shady outcrop belt. That is, deposits associated with the Shady most commonly lie low on slopes whose upper reaches are composed of older noncarbonate units. However, in the Knox belt several deposits occupy hilltops and cannot presently be supplied with manganese in this way. Several deposits in the Knox belt appear to be closely associated with faults (Stose and Miser, 1922; Cooper, 1944); in these deposits fluids in permeable gouge zones probably precipitated manganese oxides near the land surface.

Although in-place enrichment of manganese in the insoluble residue of carbonate parent rocks is the most popular hypothesis, almost nothing is known of the manganese content of the parent rocks. King and others (1944) and Rodgers (1945) present a few analyses of Shady Dolomite from Tennessee showing over 1 percent manganese, which has given some comfort to proponents of this hypothesis. Until recently, there was no reason to believe that the manganese content of these carbonate parent rocks could itself be of economic interest.

## **"PARENTAL" CARBONATE BEDROCK**

### **Shady (Tomstown) Dolomite and underlying quartzite**

The Shady Dolomite is of Early Cambrian age and is the basal carbonate unit of the Paleozoic sequence across the entire State. The unit is as much as 1,800 ft (550 m) thick. The upper portion of the unit consists mostly of massive thick-bedded dolomite with some chert, whereas the basal portion, called the Patterson Member in the southwestern part of the State, is finely banded and contains

limestone lenses and beds. The Shady overlies quartzites known as Antietam to the north of Roanoke and Erwin to the south. A transitional interval up to about 10 m thick is present in some areas, especially toward the southwest. The Patterson Member and the transitional interval are of particular interest in this report because they are spatially associated with the supergene manganese enrichments.

Exposure of the Shady Dolomite is generally poor except along river gorges and associated man-made cuts. Indeed, for a considerable portion of its outcrop length, between about Front Royal and Buena Vista, only a few exposures are known. Some of the most valuable districts of supergene manganese deposits (Elkton, Crimora, and Vesuvius-Lyndhurst) occur in this interval, and for these deposits the parent-rock material is not known. Thick residual clay occupies the position of Shady Dolomite in this geographic interval.

The depositional setting of the Shady Dolomite is predominantly a shallow-marine shelf. Pfeil and Reid (1980) took advantage of structural repetition of the unit in the Austinville area to conduct an areal facies study, which showed the presence of deeper-water slope facies toward the southeast.

The transitional zone between the basal Patterson Member of Shady Dolomite and the Antietam-Erwin Quartzite is best known in the southeastern part of the State and in the adjacent Shady Valley of Tennessee (the type area of the Shady Dolomite). The transitional zone has been described in Virginia by Stose (1942), Miller (1944), and Stose and Stose (1957), who report phosphatic and/or glauconitic, ferruginous to calcareous, fossiliferous sandstones in this interval. These authors hypothesize that the rocks of the transitional zone are an important source of manganese for supergene deposits; however, the high manganese contents reported from the Shady in adjacent Tennessee (King and others, 1944; Rodgers, 1945) are from a slightly higher stratigraphic interval.

The Antietam-Erwin Quartzite directly underlies some manganese deposits, and in some districts, such as the Glade and Lick Mountain districts (Stead and Stose, 1943; Miller, 1944), a considerable share of manganese resources occurs over this quartzite. Typically, manganese oxides in such districts occur as a matrix in brecciated quartzite.

### **Knox Group**

The Knox Group, which spans the Cambrian-Ordovician boundary, consists largely of dolomite, with some limestone units and with replacement chert throughout. The lower Ordovician part of the unit in the northern part of the State is known as the Beekmantown Dolomite.

Supergene deposits of manganese (Stose and Miser, 1922), occur over rocks of the Knox Group in Giles County and in the southwestern part of the State (fig. 1). They occur

over rocks that may be at different stratigraphic levels, and it seems possible that structural control is more important than stratigraphic control in these deposits. Near Tazewell in the southwestern part of the State, supergene manganese deposits seem most closely associated with the Upper Cambrian part of the Knox Group, known as the Copper Ridge Dolomite (Cooper, 1944).

## STUDY METHODS

Sections that are fairly complete and stratigraphically intact, located as near as possible to important districts of derived supergene manganese deposits, were collected. It was also thought desirable to collect within the same thrust sheet as the supergene deposits.

Because of a scarcity of adequate sections, only four areas of lower Shady and two of the lower Knox were collected as sections (fig. 1). Other collections from inadequately exposed or structurally complex sections are also shown on figure 1. The long geographic interval with inadequate exposure of Shady Dolomite, extending virtually from the Shenandoah River section near Front Royal to the James River sections near Buchanan, is a major limitation to this study.

Analyzed samples are all of fresh rock, trimmed of contaminated surfaces. Samples were taken at regular intervals of about 1–10 m; the interval was adjusted where necessary to include lithologic variants. Where possible, composite chip samples, representative of as much as 20 m in thickness within a relatively uniform lithologic interval, were collected for analysis. This method, which provides average values, is useful for defining anomalous intervals where background values are sufficiently low. In this study, where background manganese values were on the order of 100 parts per million (ppm), a bed containing 5 percent manganese over a thickness of only 1 m would be represented in the bulk analysis of a 20-m interval by manganese values 25 times background.

Two types of analyses were used for each sample. First, 30-element semiquantitative spectrographic analysis or 64-element emission spectrographic analysis served to determine whether unusual patterns of elemental concentration were present. Second, all samples were reanalyzed for manganese and the related elements iron, phosphorus, and barium by inductively coupled plasma (ICP) spectroscopy. The latter values are those tabulated for these four elements; the ICP analyses for manganese show slightly lower values than do the other two methods, but the manganese values obtained with different analytical methods plot against each other as straight lines with little scatter.

Analyses by spectrographic methods were by B. Arbogast and C. Skeen of the U.S. Geological Survey in Reston, and ICP analyses were by W. d'Angelo, of the U.S. Geological Survey in Reston.

**Table 1.** Manganese and other elemental contents of the Harpers Ferry section

[Mn = manganese, Fe = iron, and Ba = barium.]

Stratigraphic position	Mn (ppm)	Fe (%)	Anomalies of other elements <sup>1</sup>
<b>Antietam Quartzite</b>			
A. Uppermost exposed in rail cut	310	2.8	1,100 ppm of Ba
B. 9.1 m below A	110	3.1	1,200 ppm of Ba
<b>— Outcrop gap —</b>			
<b>Shady Dolomite</b>			
A. Lowermost exposed in rail cut	240	0.8	
B. 3.1 m above A	170	0.4	
C. 7.8–8.5 m above A	110	0.1	
D. 11.5 m above A	83	0.3	
<b>— John Brown's cave 12.4–15.3 m —</b>			
E. 14.5 m above A	95	0.4	
F. 16.3–17.1 m above A	58	0.2	
G. 22.0–22.2 m above A	120	0.6	
H. 45 m above A	37	0.1	

<sup>1</sup>Defined as concentrations relative to other samples of the same lithology, especially those of this study.

## MANGANESE CONTENTS

Analytical results are summarized by area, from northeast to southwest in each unit (fig. 1).

### Shady Dolomite and underlying quartzite Harpers Ferry area

The Antietam Quartzite–Shady Dolomite transition was examined in the Harpers Ferry area of West Virginia and Maryland, about 3 km north of Virginia, because these rocks are well exposed there. A supergene deposit of manganese oxides over Shady Dolomite was mined at Dargan, Md., about 2 km north.

A measured section was collected along the Baltimore and Ohio Railroad cuts north of the town of Harpers Ferry on the Potomac River (Charles Town quadrangle). The collection is discontinuous because of a gap in fresh rock outcrop that includes the Antietam–Shady contact. This gap appears to include over 100 m of stratigraphic section. Two samples were collected below and eight above this gap (in Antietam and Shady, respectively). The portion of Shady sampled consists toward the base of laminated limestone and toward the top of limestone with small replacement “eyes” of dolomite. Table 1 lists the results; the location of John Brown's Cave is shown to aid relocation.

The highest manganese content analyzed, 240 ppm, is from the lowest beds of the Shady Dolomite exposed in the rail cut. This lithology is a finely laminated limestone, and appears (from observations of float) to be about 30 m

**Table 2.** Manganese and other elemental contents of the Shenandoah River section

[Mn = manganese, Fe = iron, Sr = strontium, and Ba = barium.]

Meters above basal outcrop	Mn (ppm)	Fe (%)	Anomalies of other elements
0–1.0	91	0.1	3,000 ppm of Sr
4.5–5.0	77	0.1	
— Outcrop gap —			
18.0–19.0	28	0.1	
19.0–20.0	66	0.1	
24.0–25.0	32	<0.1	
— Outcrop gap 29.0–37.5 —			
39.2–39.6	120	0.1	
42.5–43.5	38	0.1	
50.5–51.5	46	0.1	
58.5–59.5	55	0.2	
64.8–65.3	62	0.2	
70.3	77	0.1	1,600 ppm of Ba

above the base of the formation. Manganese values decrease upward in the unit, except in the 22.0 to 22.2-m sample, which is siliceous.

Three samples of Shady Dolomite were also collected at the Dargan mine, to investigate the possibility that strong lateral gradients in manganese composition controlled the location of supergene deposits. These three samples contained 200 to 500 ppm manganese by spectrographic analysis (which everywhere gave higher values than ICP).

#### Shenandoah River section

The Shenandoah River exposes a section of Shady Dolomite, on the south bank, on the northern side of Calmes Neck (Ashby Gap quadrangle). No quartzite was seen in place, but the section measured by William F. Cannon and the author begins at the base of Shady Dolomite as depicted by Gathright and Nystrom (1974). This section is about 35 km southwest of the Harpers Ferry section. The nearest supergene manganese prospects, outside Front Royal about 20 km further southwest, are very lean. Table 2 shows the manganese contents of this section of Shady Dolomite. The entire measured interval consists of well-laminated to poorly laminated limestone with blebs and nodules of dolomite. The specimen at 39.2 to 39.6 m, which is the most dolomitic, contains the most manganese, 120 ppm.

#### Buchanan area

The Shady Dolomite is well exposed in the Buchanan area along the James River and in Norfolk and Western railroad cuts parallel to it. However, it appears that faulting has cut out the basal limestone unit of the Shady. Eight specimens were collected in a dolomite quarry operated by James River Limestone, Inc. ("plant 1"), about 2.5 km

east-northeast of the town of Buchanan (Buchanan quadrangle). In this quarry, the structurally lower portion of the Shady is coarsely recrystallized, massive, and veined and is in apparent fault contact with Unicoi(?) sandstone beds that are truncated by the fault. Six specimens of Shady in this area of the quarry, aggregated into three samples for spectrographic analysis, ranged from 500 to 1,000 ppm of manganese. The one nearest the fault contained 100 ppm lead, also. In the area of the weighing station, northwest of the recrystallized, massive, veined dolomite, is a structural interval of thin-bedded dolomites with stromatolites and shale partings. A composite chip sample of these beds yielded 500 ppm of manganese. At the northwest end of the quarry are dark dolomites from which a chip sample shows 200 ppm of manganese.

Four specimens were also collected along rail cuts to the northeast about 3 km, between the bridge of County Road 614 and Jennings Creek. This section is also structurally complex, and the Shady is entirely dolomitic except in a few thin intervals. These specimens, aggregated into two samples for spectrographic analysis, contain 500 to 700 ppm of manganese. One additional specimen of Shady was collected from a roadcut along nearby Bearwallow Creek, where manganese oxide forms small supergene enrichments as the cement of quartzite-clast breccia. This specimen of Shady contained 500 ppm of manganese.

#### Austinville-Ivanhoe area

Shady Dolomite is well exposed in this district, where it hosts historically important deposits of lead and zinc. Supergene manganese deposits are present in the district on Lick Mountain. The basal portions of the Shady were measured west of Fosters Falls on the east bank of the New River, in Norfolk and Western railroad cuts (Fosters Falls quadrangle). The quartzite contact is not well exposed in the rail cuts, but its position can be surmised within 10 m. The dominant lithology throughout the sampled interval is laminated carbonate, with varying ratios of calcite and dolomite, which is present as nodular clusters. Dolomitic sedimentary breccia is also present in the 13- to 18-m interval containing the highest manganese values (table 3). The three samples from 5 to 56 m above the base of the Shady gave the highest manganese values of this study, but manganese contents are nevertheless well under 1 percent. Lead and zinc values in this interval are also high. Iron content is approximately proportional to manganese content.

A subsidiary collection was made on a road cut of State Highway 54 on the north bank of the New River beside Galena Creek (Max Meadows quadrangle). In part of this exposure, dolomitic collapse breccia cuts the contact of quartzite and overlying Shady. The intact part of the exposure, toward the east, provides details of the contact not available at Fosters Falls. Table 3 shows the manganese

**Table 3.** Manganese and other elemental contents of the Fosters Falls and Galena Creek sections

[Mn = manganese, Fe = iron, Zn = zinc, Pb = lead, and P = phosphorus.]

Meters above base of Shady Dolomite <sup>1</sup>	Mn (ppm)	Fe (%)	Anomalies of other elements
<b>Fosters Falls Section</b>			
— Outcrop gap — 5–6 (approximate)	1,500	1.1	
— Outcrop gap — 13–18	3,000	2.5	850 ppm of Zn and 82 ppm of Pb
— Outcrop gap — 35–56	2,500	1.8	290 ppm of Zn and 120 ppm of Pb
— Outcrop gap — 65–85	450	0.3	
85–103	250	0.2	
<b>Galena Creek Section</b>			
Stratigraphic relation to contact zone			
3–7 m below	620	3.6	0.09% P
0–3 m below	500	3.4	
1.8-m contact zone	1,300	2.5	
0–3 m above	1,100	1.4	

<sup>1</sup>Measurements are corrected for dip.

contents of these rocks. Within the 10 m of section, chloritic to glauconitic quartzite passes upward through glauconitic granular sand interbedded with dolomite and laminated shale, into massive dolomite, apparently bioturbated. Neither manganese nor lead-zinc contents are as high as at Fosters Falls. Manganese shows a maximum in the transition beds. Some phosphate apparently accompanies glauconite.

### Marion area

The Glade Mountain district of supergene manganese deposits, south of Marion, was the most recent significant producer of manganese in the State. I was not able to find an adequate section of the Antietam-Erwin Quartzite and the lower Shady on Brushy Mountain, where the largest deposits occur, but had to content myself with a short section across the Shady contact in the Rye Valley, to the

**Table 4.** Manganese and other elemental contents of the Sugar Grove section

[Mn = manganese, Fe = iron, Ba = barium, and P = phosphorus.]

Stratigraphic relation to contact zone	Mn (ppm)	Fe (%)	Anomalies of other elements
0–3 m below	810	2.6	1,400 ppm of Ba
1-m contact zone	930	2.2	0.09% P
0–3 m above	960	1.3	
3–6 m above	700	1.0	

south. This section is near Sugar Grove, in the banks of Dickey Creek, along County Road 16, near Saltpeter Cave (Atkins quadrangle). The exposed transition is from fine laminated quartzite, through glauconitic quartzite and dolomites, to whitish dolomite with calcareous lenses. Manganese contents, shown in table 4, show a very slight maximum, below 0.1 percent, just above the contact.

### Summary

Analyses of four stratigraphic sections across the Shady Dolomite and underlying quartzite suggest that manganese contents reach a maximum in the lowermost Shady throughout Virginia. This corresponds to the stratigraphic interval on which supergene enrichments occur and supports the hypothesis that the manganese enrichments derive from the rocks on which they rest. However, none of the sedimentary rocks analyzed from this interval show manganese contents of even 1 percent. Thus these rocks themselves are of no economic interest.

The average manganese content of the 24 samples analyzed by ICP from the Shady and underlying quartzite is 490 ppm. The average content differs little between Shady and quartzite samples. Manganese content is roughly proportional to iron content in samples of Shady Dolomite (fig. 2) both within individual sections and as an entire array. The highest manganese/iron ratios are about 0.15, suggesting that fractionation of iron and manganese, necessary to form valuable manganese concentrations, was not occurring in this sedimentary environment.

The degree of manganese enrichment required to form a typical supergene concentration from average parent rocks is about 800 times in this area. To contend that all this enrichment has resulted only from weathering strains one's credibility. Other insoluble elements normally enriched in weathering profiles, for example, iron and aluminum, have not been enriched to the same degree. Iron in the analyzed parent carbonate rocks ranges from 0.04 percent to 2.5 percent, and averages 0.6 percent. Alumina (from semi-quantitative spectrographic analyses) ranges from 0.6 percent to 6.2 percent, and averages 2.2 percent. The enrichment required to make a supergene concentration of typical composition from average Shady is only about 13 times for iron and 1.4 times for aluminum. This reasoning suggests that enrichment of manganese in supergene deposits extends beyond simple residual enrichment.

Further enrichment may have taken two forms:

1. Preferential enrichment of manganese by geochemical trapping in the supergene environment. This hypothesis is essentially that proposed by Hack (1965). Manganese carried in solution by ground water from a variety of sources (including immediately underlying rocks) would preferentially be precipitated in supergene deposits over rocks that alter the geochemical environment of the ground water.

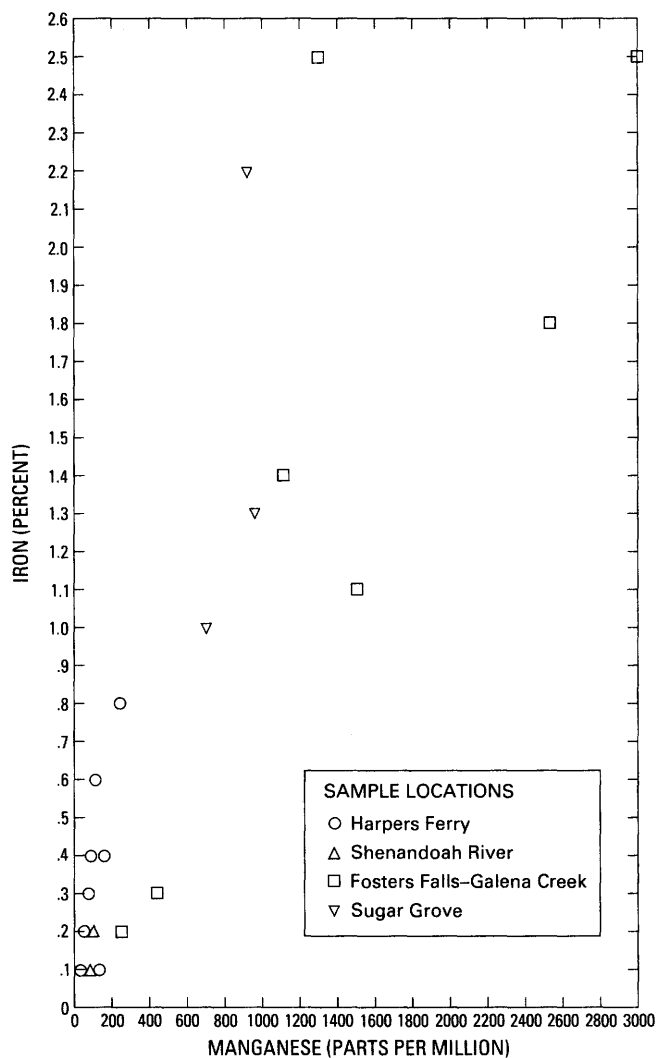


Figure 2. Manganese and iron contents (by inductively coupled plasma analysis) of samples of Shady Dolomite.

- Enrichment of manganese relative to other elements, especially aluminum, as concretions and small orebodies within the supergene deposit. Exposures of some of these deposits certainly suggest local enrichment, as the distribution of manganese is extremely inhomogeneous, and the tonnage of manganese ore is a small percentage of the tonnage of residual material. That is, some enrichment occurred in the formation of the weathered overburden as a whole, and further enrichment occurred to form ore-grade bodies.

## Knox Group

The largest supergene manganese deposits over rocks of the Knox Group are in the southwestern part of the State

Table 5. Manganese and other elemental contents of the New River section, Knox Group

[Mn = manganese, Fe = iron, Cr = chromium, Ni = nickel, Pb = lead, Cu = copper, and Mo = molybdenum.]

Meters above base of Knox Group <sup>1</sup>	Mn (ppm)	Fe (%)	Anomalies of other elements
10	86		
26	110	0.1	
110	88		
235	100	0.5	200 ppm of Cr, 70 ppm of Pb, 50 ppm of Ni and Cu, and 10 ppm of Mo
365-470	88	0.5	
496	43		
550	86		
600	85		

<sup>1</sup>The Knox Group is 650-m thick here.

(fig. 1). Sampling was therefore concentrated in that region, except for a reconnaissance investigation at the northernmost known prospect.

## Round Hill

The Scott prospect is atop Round Hill, near Strasburg between Interstate Highway 81 and U.S. Highway 11 (Toms Brook quadrangle). Manganese concretions at the Scott prospect are iron-rich and cherty and, therefore, not of economic interest. Underlying Beekmantown Dolomite is not well exposed. Two short chip samples collected on County Road 651 for spectrographic analysis contained 100 and 500 ppm of manganese. No other elemental concentrations were of interest.

## New River section

Several supergene manganese deposits in the Newport area of Giles County are on dolomite of the Knox Group, and the nearby New River section was, therefore, sampled to establish the composition of the dolomite. Sampling was conducted along the Norfolk and Western railroad cuts south of Goodwins Ferry (Eggleston quadrangle). Sampling was keyed to an unpublished section measured by A.T. Ovenshine, incorporated in table 5. Lithologies are mostly dolomitic, with a few limestone horizons up to about 10-m thick (one at 496 m). Laminated, bioturbated, and oolitic horizons are present. Chert nodules are present in many beds. The specimen at 235 m, with high base metal contents, is a dark, shaly dolomite. Manganese contents of all the analyzed rocks are low.

## Tazewell area

A section at Wittens Mills (Tiptop quadrangle) was sampled (table 6) in order to assess the composition of the

**Table 6.** Manganese and other elemental contents of the Wittens Mills section, Knox Group

[Mn = manganese, Fe = iron, Zn = zinc, and Pb = lead.]

Meters above base of Copper Ridge Dolomite	Mn (ppm)	Fe (%)	Anomalies of other elements
40–49.8 — Outcrop gap —	160	0.1	
52.4–60.5	130	0.1	
60.5–65.7	200	0.2	
65.7–83.7	130	0.2	410 ppm of Zn and 95 ppm of Pb
83.7–108.8 — Outcrop gap —	190	0.2	
143.4–154.7	180	0.2	
154.7–168.1	170	0.3	
168.1–185.8	150	0.3	
185.8–187.2	140	0.5	

Copper Ridge Dolomite, locally the basal formation of the Knox Group. These rocks apparently underlie supergene manganese enrichments 3–4 km northeast. The section was composite, measured partly along County Road 651 and partly along the Norfolk and Western railroad cuts. An outcrop gap represents about 100 m of section. All the beds are dolomitic, and most are either laminated micrites or massive arenites that are locally oolitic. Shaly layers, shellbeds, and intraformational conglomerates are present. The 65.7- to 83.7-m interval with high lead and zinc content consists of two lithologies, one of fine dolomites with algal laminae and the other of oolites replaced by chert.

### Summary

The analyzed rocks of the Knox Group contain an average of 125 ppm manganese, probably too little to explain the supergene manganese deposits on them by simple residual enrichment. The supergene manganese enrichments on the Knox typically occur as cement of chert-fragment breccia, and are closely associated with the surface traces of the Saltville and related faults. These facts suggest that a fault-related plumbing system is more important in manganese supply than is the composition of carbonate rocks in forming supergene deposits on the Knox. Indeed, even rather fresh specimens of fault breccia along the Saltville fault contain manganese in the vicinity of Newport (Art Schultz, U.S. Geological Survey, oral commun., 1987). Precipitation reactions controlled by carbonate rocks may have determined the locus of manganese deposition both at depth and at the surface.

### CONCLUSIONS

The manganese contents of lower Paleozoic carbonate rocks of Virginia are too low to explain the supergene manganese deposits developed on them solely as residual

enrichments. The manganese contents of the carbonate rocks are typically about 100–500 ppm, and high values range up only to 3,000 ppm, or 0.3 percent. In the deposits over Shady Dolomite and underlying quartzite, it is likely that manganese has been trapped in overburden by the increased alkalinity of ground water over the carbonate rocks. In the deposits over the Knox Group, it is likely that ground water moving along faults has brought manganese into the overburden. In both cases, further concentration within the overburden geochemical system has resulted in the small, high-grade bodies that were mined.

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Chapter B

# Manganese Contents of Some Rocks of Silurian and Devonian Ages in Northwest Virginia

By LESLIE J. COX

A presentation of geochemical data  
from measured sections of sedimentary rocks  
of Silurian and Devonian ages  
that underlie supergene manganese deposits  
in northwest Virginia

U.S. GEOLOGICAL SURVEY BULLETIN 1916

MANGANESE CONTENTS OF SOME SEDIMENTARY ROCKS OF PALEOZOIC AGE  
IN VIRGINIA



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## CHAPTER B

# Manganese Contents of Some Rocks of Silurian and Devonian Ages in Northwest Virginia

By Leslie J. Cox

### Abstract

The lower Paleozoic carbonate formations that form the substrate of supergene manganese deposits in Virginia have an apparent potential for manganese resources in shallow-marine sedimentary deposits. Those formations of Silurian and Devonian ages that form the substrate of supergene manganese deposits in northwest Virginia were analyzed for manganese and other elements in this reconnaissance investigation. The rocks were found to generally contain only 100 to 400 parts per million (ppm) of manganese. However, manganese contents as high as 0.15 percent were found in the silicified and fractured limestone beds of the upper Helderberg Group near Liberty Furnace, Va. The higher concentrations of manganese in these altered rocks are attributed to incipient, in-place weathering of rocks that may have had manganese-rich carbonate cement prior to local destruction of original fabrics.

Upper Helderberg Group limestones contain zones of manganese-rich carbonate cements fixed in geographic distribution by the distances meteoric ground waters traveled from recharge areas exposed in Devonian time (Dorobek, 1987). There may be a correlation between the location of residually concentrated manganese in the study area and the paleo-zone traversed by reduced meteoric ground waters.

### INTRODUCTION

The manganese resources in Virginia consist of supergene concentrations of manganese oxides, which lie above folded sedimentary rocks of Paleozoic age in the Valley and Ridge Province of the Central Appalachian Mountains. The supergene deposits of Virginia were an important source of domestically produced manganese from

before the Civil War (as early as the mid 1830's) until after World War II (as late as the late 1950's). The largest share of manganese came from the supergene deposits over carbonate rocks of Early Cambrian age. Lesser amounts were extracted from deposits over dolomites of Cambrian-Ordovician age and limestones of Middle Devonian age.

Throughout the 1900's, exploration for manganese resources in Virginia was directed toward the discovery of additional supergene deposits. Although the favored hypothesis of origin for the supergene deposits was in-place enrichment of manganese in the insoluble residue of carbonate parent rocks, little was reported about the manganese contents of the parent rocks.

The potential for significant primary (sedimentary) concentrations of manganese in Virginia remained unexplored until Force (this report, Chapter A) suggested that the lower Paleozoic carbonate formations beneath the supergene deposits were permissive for shallow-marine sedimentary manganese deposits. Guided by the hypothesis that the distribution of supergene manganese concentrations might reflect a similar distribution of inconspicuous yet significant manganese concentrations in the parent rocks, Force (this report, Chapter A) undertook a systematic reconnaissance exploration of the rocks of Cambrian and Ordovician age in Virginia in order to document their manganese contents.

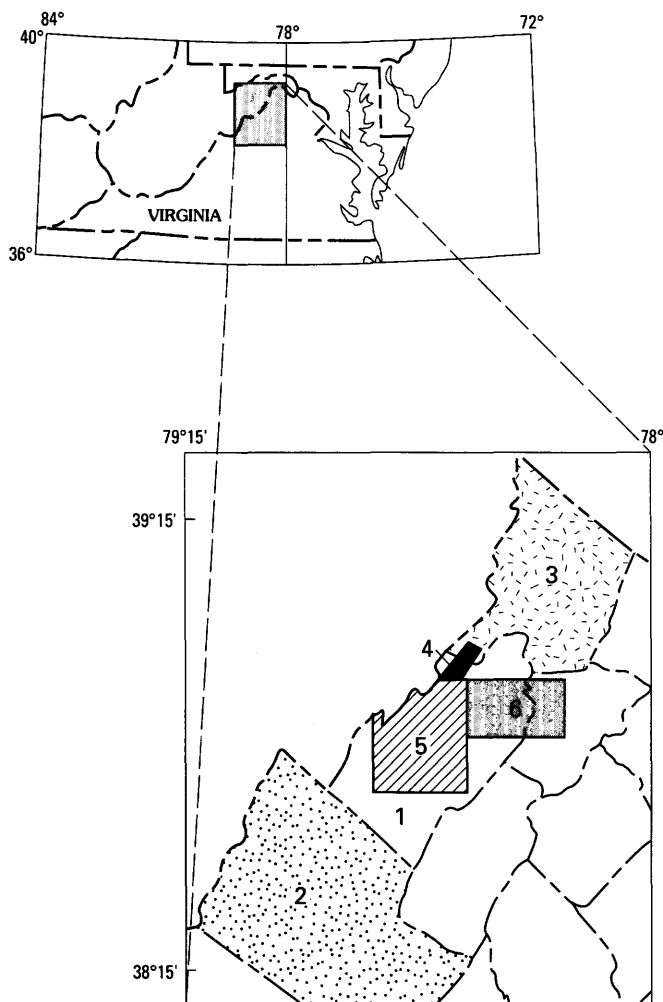
This study investigates the manganese contents of the Devonian hosts of the supergene manganese deposits in the vicinity of Cedar Creek Valley in northwest Virginia (fig. 1).

### Mining in the study area

The supergene manganese deposits and occurrences lie over the tightly folded rocks of the Helderberg Group of Upper Silurian-Lower Devonian age and the Ridgeley Sandstone of Devonian age (fig. 2). The manganese ore

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**Figure 1.** Index of geologic maps of the study area. Map references are keyed by number: 1, Calver and Hobbs (1963), (scale 1:500,000 (clear area only); 2, Brent (1960), scale 1:62,500 (stippled area); 3, Butts and Edmundson (1966), scale 1:62,500 (stippled area); 4, Monroe (1942), scale 1:24,000 (shaded area); 5, Young and Rader (1974), scale 1:24,000 (ruled area); and 6, Rader and Biggs (1976), scale 1:24,000 (shaded area).

minerals occur in the residuum of the uppermost limestone beds of the Helderberg Group and in the open spaces of fractured Ridgeley Sandstone, which lies above the limestones of the Helderberg Group. The residuum consists of variable amounts of yellow sandy clay, cherty clay, clay, and ore.

The production of manganese oxide ore in Cedar Creek Valley began with the opening of the Mineral Ridge mine (fig. 2, locality *a*) in 1834; the Godlove, Bonnet Hill, and Capola Mountain mines (fig. 2, localities *b, c*, and *d*), were opened in 1847, 1848, and 1880, respectively (Stose and Miser, 1922). In the same era, manganese oxides were mined from the High Head prospects (fig. 2, locality *e*) in the Stony Creek drainage basin. These deposits were mined

intermittently until the early 1920's; several were reopened in 1940 (McGill, 1936; Monroe, 1942). Production at the Mineral Ridge mine ceased in 1957 (Butts and Edmundson, 1966). The ore was taken from depths as great as 200 ft (Stose and Miser, 1922), but more typically from depths less than 100 ft. None of these deposits are mined today. Detailed information on each mine and prospect in the Cedar Creek Valley manganese district is given by Stose and Miser (1922) and Monroe (1942).

## Depositional setting of the Helderberg Group and Ridgeley Sandstone

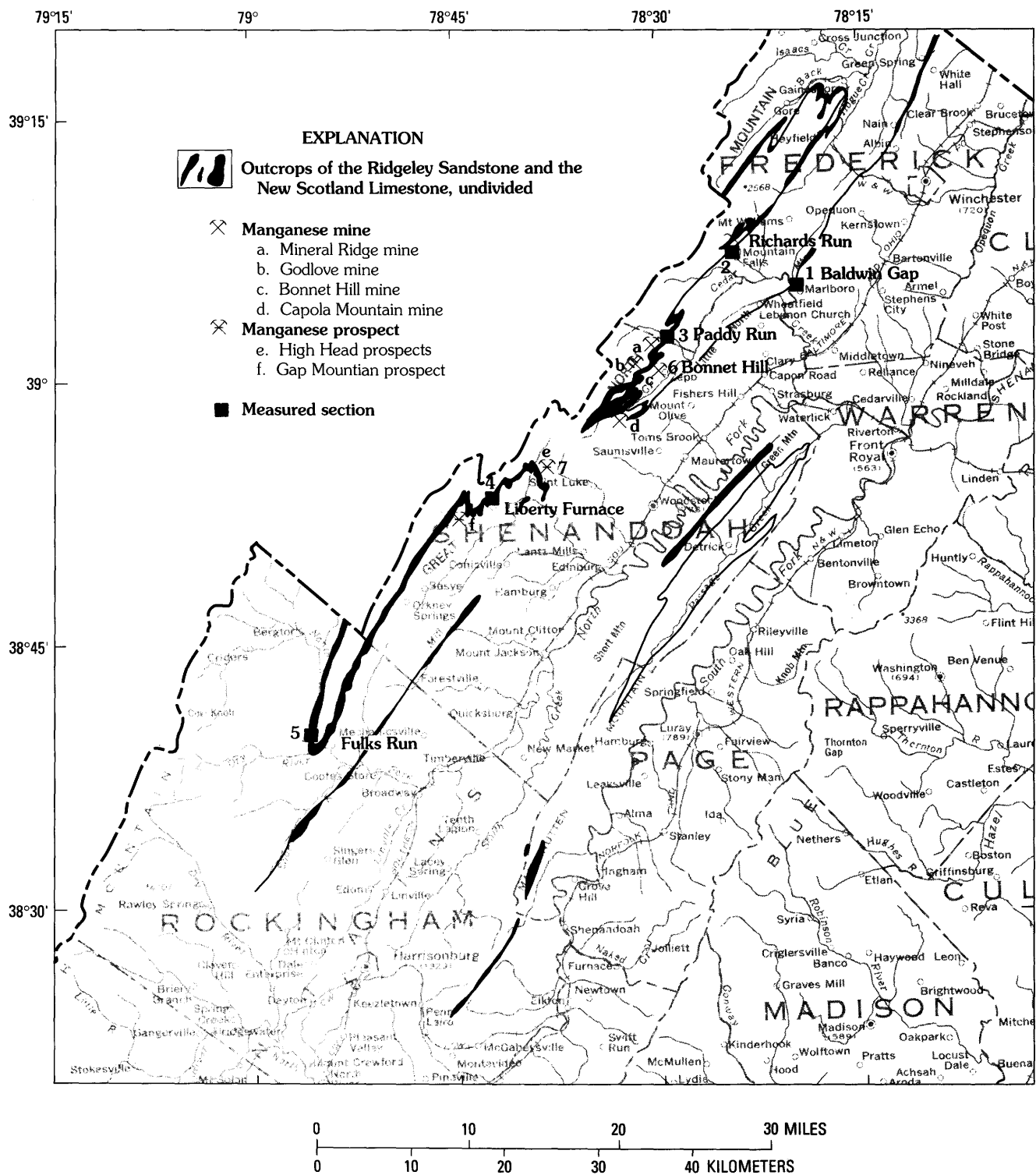
In Silurian and Devonian time the Appalachian basin extended northeast through what is now Virginia–West Virginia–Maryland. Tectonic highlands of low relief bordered the eastern side of the central Appalachian foreland basin. A sequence of mixed siliciclastic-carbonate sediments, the Helderberg Group, were deposited on a gently sloping, carbonate ramp that was built westward from the tectonic highlands (Dorobek and Read, 1986).

At the time of the last and uppermost transgressive sequence of Helderberg Group deposition, described by Dorobek and Read (1986), the deepest part of the basin lay northwest of the study area. There, the dark color and fossil content of the Mandata Shale indicate that the water was oxygen-depleted (Dorobek and Read, 1986). Limestones indicative of shallower, above-wave base, oxygenated water were deposited near the basin edge east and south of the study area. Between the deepest part of the basin and the shore, nodular-bedded, shaly, and cherty limestones were deposited below fair-weather wave base in the less-oxidizing conditions of the deep-ramp setting (Dorobek and Read, 1986). These limestones are known as the New Scotland Limestone (Young and Rader, 1974) in the study area and as the Corriganville Limestone and Lower Licking Creek Formations (Dorobek and Read, 1986) south of the study area (fig. 3). The depositional setting described above for the Appalachian basin in the Middle Devonian (apparent oxygen stratification and carbonate deposition at a time of high sea level stand (transgression)) indicate that the deep-ramp sediments are broadly permissive for shallow-marine manganese deposits as modeled by Force and Cannon (1988).

At the onset of the Acadian orogeny, Middle Devonian clastics and bioclastics (Ridgeley Sandstone, Huntersville Chert, and Needmore Shale) spread westward and buried the Helderberg Group. The New Scotland Limestone

**Figure 2.** Outcrop map showing the locations of Lower and Middle Devonian formations, manganese mines in Cedar Creek Valley, prospects near Liberty Furnace, and the sections sampled in north-west Virginia. ►





**Sample localities**—with 7.5-minute quadrangle map coverage and references for previously measured sections

1. **Baldwin Gap**—Middletown quadrangle, Va. Webb and Nunan (1972, p. 60 and 64); Butts and Edmundson (1966, p. 52); and Swartz (1929, p. 60-61) (Note: Swartz (1929) erroneously referred to this location as Fawcett Gap).
2. **Richards Run**—Mountain Falls quadrangle, Va.-W.Va. Webb and Nunan (1972, p. 60 and 64); Butts and Edmundson (1966, p. 56-57).
3. **Paddy Run**—Mountain Falls quadrangle, Va.-W.Va. In Paddy Run, east of the bridge on State Route 600, 2.8 miles northeast of Zepp.
4. **Liberty Furnace**—Wolf Gap quadrangle, W.Va.-Va. In Laurel Run, 0.4 miles north of the intersection of State Routes 717 and 691, at Liberty Furnace.
5. **Fulks Run**—Fulks Run quadrangle, Va. Webb and Nunan (1972, p. 118-119); Swartz (1929, p. 62); Woodward (1943, p. 201-202); and Woodward (1955, p. 9-10).
6. **Bonnet Hill**—Wardensville quadrangle, W.Va. Located 0.7 miles northwest of Zepp.
7. **High Head Prospects**—Wolf Gap quadrangle, W. Va.-Va. Location published in Stose and Miser (1922, p. 90)

Dorobek and Read (1986)				Diecchio (1985)		Young and Rader (1974)	
WESTERN MARYLAND		SOUTHWEST VIRGINIA		SOUTHWEST VIRGINIA		NORTHWEST VIRGINIA	
LOWER AND MIDDLE DEVONIAN	ULSTERIAN	Needmore Shale	Huntersville Chert Needmore Shale	HELDERBERG GROUP	HELDERBERG GROUP	HELDERBERG LIMESTONES ?	Needmore Formation
		Oriskany Sandstone	Oriskany Sandstone				Ridgeley Sandstone
		Shriver Chert Mandata Shale	Licking Creek Limestone				New Scotland Limestone
		Corriganville Limestone	Corriganville Limestone Healing Springs Sandstone				
		New Creek Limestone Elbow Ridge Sandstone	New Creek Limestone				New Creek Limestone
	CAYUGAN	Keyser Limestone	Upper Keyser Limestone Clifton Forge Sandstone Big Mountain Shale Lower Keyser Limestone				Keyser Formation
Tonoloway Limestone		Tonoloway Limestone	Tonoloway Limestone				

**Figure 3.** Regional chronostratigraphic correlation chart showing rocks of Cayugan and Ulsterian age in the central Appalachian basin (Young and Rader, 1974; Diecchio, 1985; Dorobek and Read, 1986).

is overlain by the Ridgeley Sandstone of the Oriskany Group in southwest Virginia and western Maryland. The Oriskany (Ridgeley) Sandstone is a near shoreline deposit (Dorobek and Read, 1986). The limestone-sandstone contact is observed in Richards Run and Fulks Run (fig. 2).

The contact between the New Scotland and underlying Keyser Limestone of Silurian age is obscured at each locality sampled for this study. The Keyser Limestone is represented by deep ramp limestone or carbonate tidal flats (Dorobek and Read, 1986).

### Theories on the origins of supergene manganese concentrations over rocks of Devonian age in Virginia

Hack (1965) best described the geochemical restrictions applicable to the manganese oxides in the weathered mantle over carbonate rocks in northwest Virginia. A brief summary of Hack, 1965, p. 70–76, follows: Manganese oxides and hydroxides can exist as solutes in fresh rain or stream water having an Eh of 0.3–0.5 and pH of 5.0–6.5. Where fresh water encounters carbonate rock, the carbonate dissolves and the alkalinity and the pH of the water rise. If the pH rises to 7 or the Eh drops below 0.3, the manganese oxides and hydroxides can no longer remain in solution and precipitate out in the developing residuum of the host rock.

Manganese phases already present in the carbonate rock exposed to weathering would also be trapped as insoluble residue in the alkaline geochemical environment.

All theories on the origins of supergene manganese deposits in Virginia to date regard the host rocks as either (1) deposition sites into which the manganese is brought and trapped or (2) as the parent rocks within which manganese is disseminated prior to in-situ weathering. There is growing evidence that the carbonate rocks of Cambrian and Ordovician ages may be regarded as deposition-site hosts (Force, this report, Chapter A), whereas the carbonate rocks of Devonian age may be parent rocks to the overlying manganese deposits.

Parent rocks enriched in manganese by shallow-marine processes might give rise to supergene deposits constrained to the stratigraphic positions that had been occupied by the primary concentrations. So constrained are the supergene deposits in Cedar Creek Valley to the stratigraphic position occupied by the Upper Helderburg Group that Butts and Edmundson (1966) recommended: “since the proven occurrence of manganese in southwestern Frederick County occurs within the decomposed New Scotland Limestone immediately under the Oriskany Sandstone, any additional search or prospecting for manganese should first be restricted to areas where these rocks are present.” Equally stringent stratigraphic limitations are not imposed on manganese deposits hosted by rocks that are

enabled, largely by their geomorphological setting and carbonate make-up, to serve as deposition sites for manganese solutes in ground water.

In Cedar Creek Valley the manganese mines are near the crests of low hills, 200–400 ft above the lowland of the valley (Monroe, 1942). Their hilltop positions preclude access to manganese sources from above, unlike the deposits over carbonate rocks of Cambrian age in the Shenandoah Valley (Hack, 1965).

Hewett and others (1918) proposed that the source of manganese for residual deposits came from a widely disseminated carbonate phase in the dolomites and limestones, and possibly in the silicate phases in other rock types. No more specific mineral or rock sources were subsequently identified until recently, when zones of manganese-rich carbonate cements were identified by Dorobek (1987) in the Helderberg Group sediments.

Dorobek (1987) noticed that differences in the luminescent properties of the carbonate cements in Helderberg Group limestones correspond to large differences in manganese content. Updip, brightly luminescent cements contain an average of 1,164 ppm of manganese (Dorobek, 1987); this is greater than 50 times as much manganese as in basinward, nonluminescent cements. Dorobek (1987) proposed that the geographic distribution of the manganese-rich cements was determined by the distances meteoric ground waters traveled (as far as 90 mi) from the recharge areas on the eastern shore of the Appalachian basin in Devonian time. The cross section in figure 4 is taken from figure 11 in Dorobek (1987), which shows the basinward extent of brightly luminescent (manganese-rich) cements.

It is likely that parent-rock hosts of manganese deposits are associated with fewer structural and geomorphological settings than are the deposition-site hosts of manganese. The association of some deposits of Ordovician age with major faults, for example, suggests that the plumbing system is more important than the composition of the parent rocks in supplying manganese to the area (Force, this report, Chapter A). For the manganese deposits hosted by rocks of Cambrian age on the east side of the Shenandoah Valley, at the foot of the Blue Ridge, Hewett and others (1918) recognized at least five types of structural settings. Each serves as a favorable channel for ground-water circulation. Near-surface (<300 ft) structural troughs of carbonate rock underlain by quartzite were thought superior to faults as favorable channels (Hewett and others, 1918).

Only one structural setting is described by Stose and Miser (1922) for the ores hosted by rocks of Devonian age in Cedar Creek Valley. There the deposits are especially numerous in areas where the limestones are repeated in synclinal folds that have brought the Devonian beds to the surface. Close folding appears to have shattered the rocks and created the fractures in the sandstones that the manganese oxides fill (Stose and Miser, 1922; Monroe, 1942).

Tightly folded rocks have more fractures through which solutions, important to the dissolution of the host rock, can circulate freely.

Deposits of manganese oxides parallel to bedding have also been recognized in steeply dipping Ridgeley Sandstone (Holden, 1936; Monroe, 1942; Young and Rader, 1974). One expects that meteoric ground water traveling through permeable sandstone with manganiferous calcite cement will residually concentrate the manganese by the same geochemical processes as when it meets manganiferous carbonate cement in quartz-silty limestone.

## METHODS OF STUDY

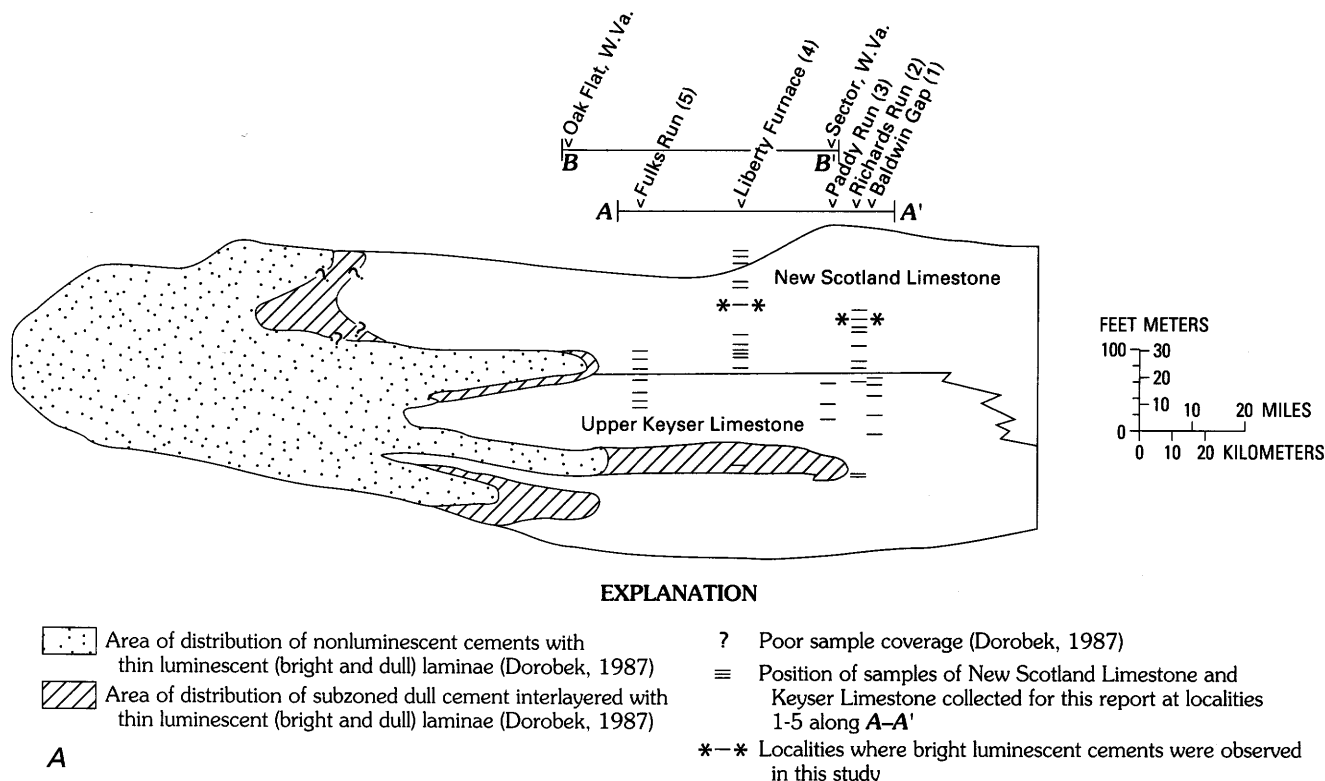
### Field methods

One hundred and two samples of limestone, chert, sandstone, and shale of Silurian and Devonian ages were collected from sections along strike from supergene manganese mines and prospects (fig. 2). Samples of unweathered Ridgeley Sandstone and New Scotland Limestone (uppermost in the Helderberg Group) were sought in particular. The best exposures were found in stream and roadside outcrops.

Nearly complete sections were found at least 3 mi from the manganese mines. Samples of Ridgeley Sandstone, New Scotland Limestone, and Keyser Limestone were collected from the sections measured at Liberty Furnace (fig. 2, locality 4; fig. 5A), Fulks Run (fig. 2, locality 5; fig. 5B), and Richards Run (fig. 2, locality 2; fig. 5C).

Sampling of sections nearest the manganese deposits was incomplete because of the poor exposure of New Scotland Limestone. Samples of Romney Shale, rusty Ridgeley Sandstone, and Keyser Limestone were collected less than 3,000 ft north of the Mineral Ridge mine in Paddy Run (fig. 2, locality 3; fig. 5D), where a covered interval, 225 ft wide, represents the New Scotland Limestone. Samples of Ridgeley Sandstone and Keyser Limestone were collected near the Bonnet Hill mine (fig. 2, locality c), 0.7 mi northwest of Zepp. Three samples of Keyser Limestone were collected near the High Head prospects (fig. 2, locality e), 2.3 mi northwest of Columbia Furnace (fig. 2). Samples of the Keyser and Tonoloway Limestones were collected at Baldwin Gap (fig. 2, locality 1; fig. 5E).

Samples for chemical analyses were collected from each section so as not to miss any bed that might be at least 3 ft thick and have >1 weight percent manganese. Most sandstone samples were of single rocks representative of 1- to 5-ft thicknesses of section. Most limestone samples were composites of 2–7 fresh chips taken over 10- to 20-ft-thick intervals, with each chip representing an apparently homogeneous interval of about 3–5 ft of exposed rock. Background concentrations near 130 ppm manganese were anticipated in the limestone and sandstone samples on the



**Figure 4.** Restored stratigraphic section (A) showing relative locations of studied sections (this report) and cathodoluminescent zonation of Dorobek (1987). Locations of sections from this study are superimposed on a cross section of the regional distribution of cathodoluminescent cement zones determined by Dorobek (1987, section E-E', fig. 11, p. 505) which passes through Oak Flat, Petersburg Gap, and Sector, W. Va., approximately 25 mi west of the study area. Map (B) showing the locations of measured sections along E-E' and A-A'. Sector, W. Va., is 25 mi N 55 °W of the Paddy Run location.

manganese (>300 ppm), thereby bringing attention to the sampled interval.

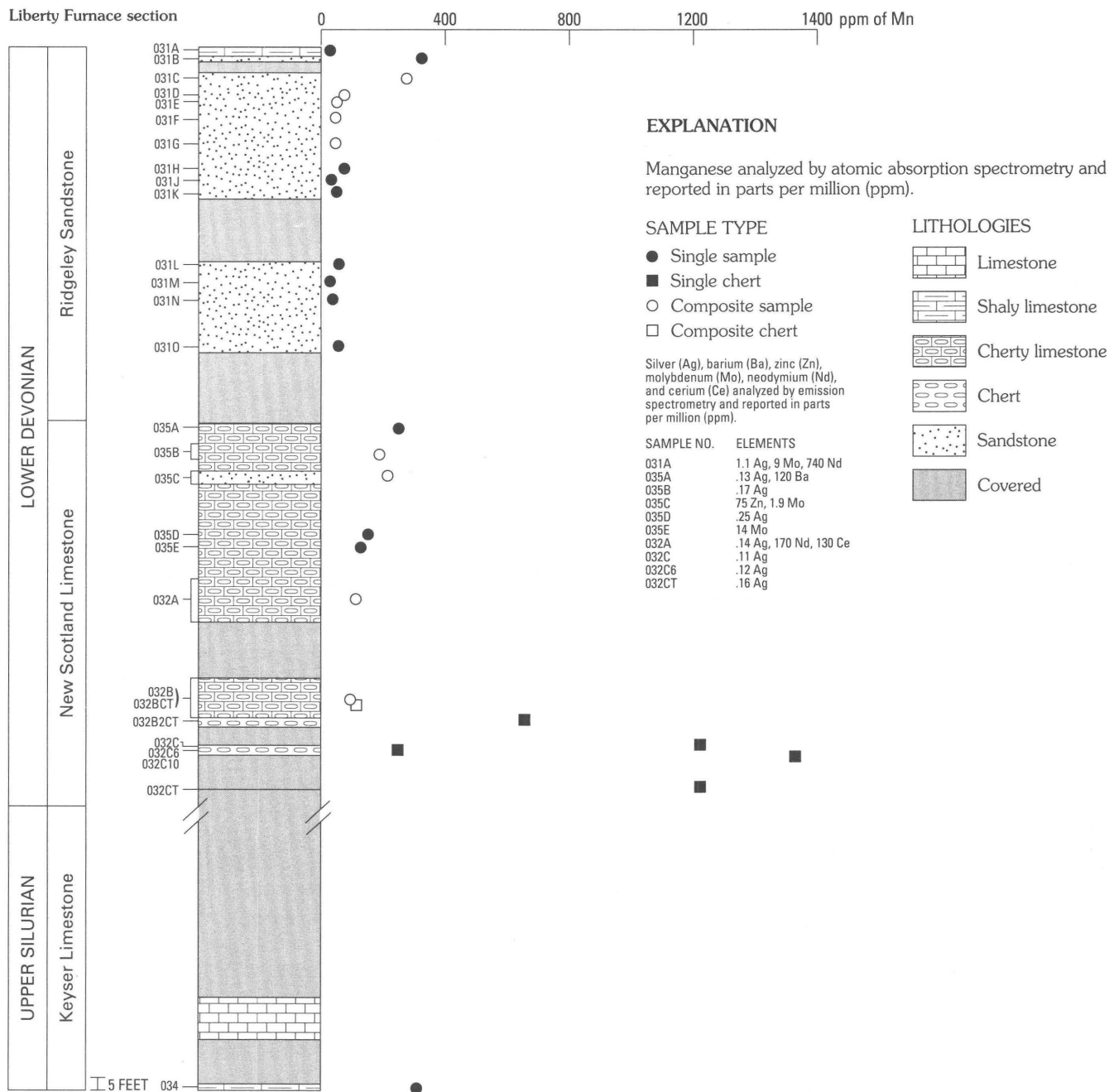
## Analytical methods

Semiquantitative spectrographic analyses for 64 elements and quantitative inductively coupled plasma (ICP) spectrographic analyses for manganese, iron, barium, and phosphorous were completed in U.S. Geological Survey laboratories (Reston, Va.) for the 102 rock samples. This report contains the analytical data on 41 of the chemical elements (table 1).

## Petrographic methods

Nine samples were studied with a petrographic microscope. Five of the samples were of Ridgeley Sandstone from the Richards Run, Paddy Run, and Liberty Furnace sections. Three of the samples were of New Scotland Limestone from Fulks Run (sample 053C, fig. 5B),

basis of analyses reported by McCue and others (1939) for equivalent rocks in West Virginia. With such low-level background values, a composite sample composed of at least one chip from a bed with greater than 0.1 weight percent manganese and no more than six chips with 0.01 weight percent would probably contain a noticeable level of



**Figure 5A–E.** Chronostratigraphic and lithostratigraphic sections of Paleozoic rocks in Virginia at Liberty Furnace, Fulks Run, Richards Run, Paddy Run, and Baldwin Gap, showing the manganese contents of the intervals sampled. Stratigraphic nomenclature applies to rocks in northwest Virginia.

Figure 5A. Section at Liberty Furnace.

Richards Run (sample 012B, fig. 5C), and Liberty Furnace (sample 032A, fig. 5A). One sample was of chert containing 1,200 ppm of manganese from Liberty Furnace (sample 032C, fig. 5A).

Highly polished sections were obtained of samples 012B, 032A, and 032C to look at opaque and carbonate phases with the reflected light objectives on a petro-

graphic microscope and the scanning electron microscope (SEM). The SEM was operated with the assistance of Elaine McGee (U.S. Geological Survey). Cathodoluminescence petrography was also done to look for brightly luminescent cements with a luminoscope, which was operated with the assistance of Jim Goss (U.S. Geological Survey).

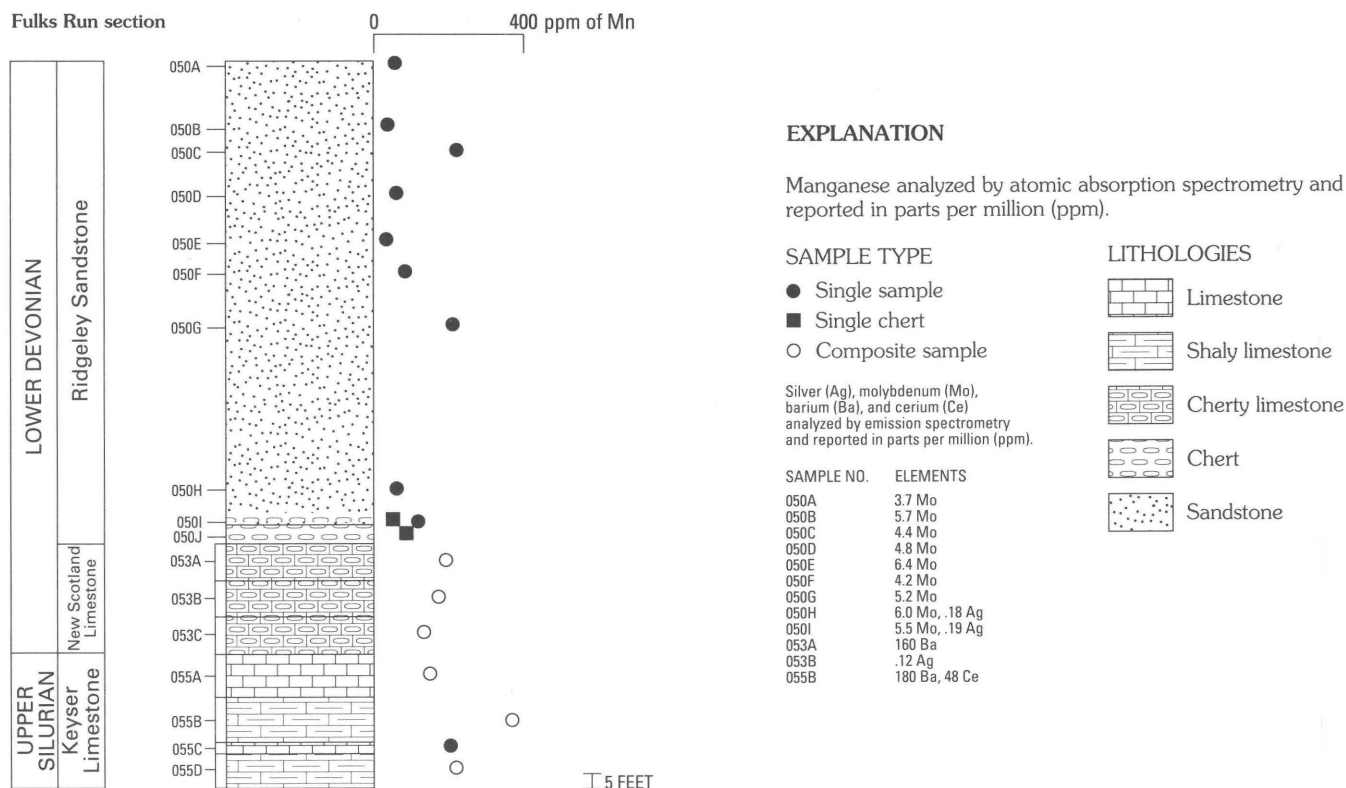


Figure 5B. Section at Fulks Run.

## RESULTS OF CHEMICAL ANALYSES

### Manganese contents at each section (north to south)

At Baldwin Gap (fig. 5E) manganese contents of the Keyser and Tonoloway Limestones of Silurian age are uniformly near 200 ppm for 260 ft of stratigraphic thickness in the upper part of the section. In the lower third of the section the manganese content averages 460 ppm where silty and cherty beds in the Tonoloway Limestone are encountered.

At Richards Run (fig. 5C) manganese contents are highest in Romney Shale (290–480 ppm) and less than 250 ppm in the section below the Romney Shale. Chert samples of the New Scotland Limestone contain only half (63, 69, and 24 ppm) the manganese of the limestone (120 ppm) wherever adjacent samples were collected in the section.

At Paddy Run (fig. 5D) manganese contents are highest in samples collected at the contact of Ridgeley Sandstone (640 ppm in sandstone) with Romney Shale (1,600 ppm in shale). These samples are weathered and red from oxidized iron; the sandstone is brecciated at the contact. In contrast, unweathered, nonbrecciated sandstone 28 ft below the contact contains only 17 ppm of manganese.

At the Liberty Furnace section (fig. 5A) most samples contain less than 400 ppm of manganese, but the basal chert

beds of the New Scotland Limestone contain 650–1,500 ppm of manganese. These rocks are described in greater detail in the section titled “Manganese contents in the rocks of the Liberty Furnace section.”

At Fulks Run (fig. 5B) manganese contents are all below 400 ppm. As at Richards Run, interbeds of chert contain less manganese than the limestone beds.

### Manganese contents by lithology

The ranges of manganese contents for limestones from the Keyser (20 samples) and New Scotland (16 samples) Limestones are similar, from 81 to 360 ppm for the former and from 90 to 240 ppm for the latter. The Keyser Limestone has a mean manganese content of 187 ppm (with one standard deviation of 68 ppm). This mean varies from section to section; for example, the mean is 137 ppm in the north at Richards Run and is 225 ppm in the south at Fulks Run (fig. 2). The variation probably reflects the diversity of depositional environments represented by the Keyser Limestone. The mean manganese content of New Scotland Limestone is 152 ppm (with one standard deviation of 45 ppm) and is fairly consistent for each section sampled.

Petrographic examination revealed that the high silica (>11 weight percent, table 1) New Scotland limestones, between chert beds at Fulks Run and Richards Run, are free

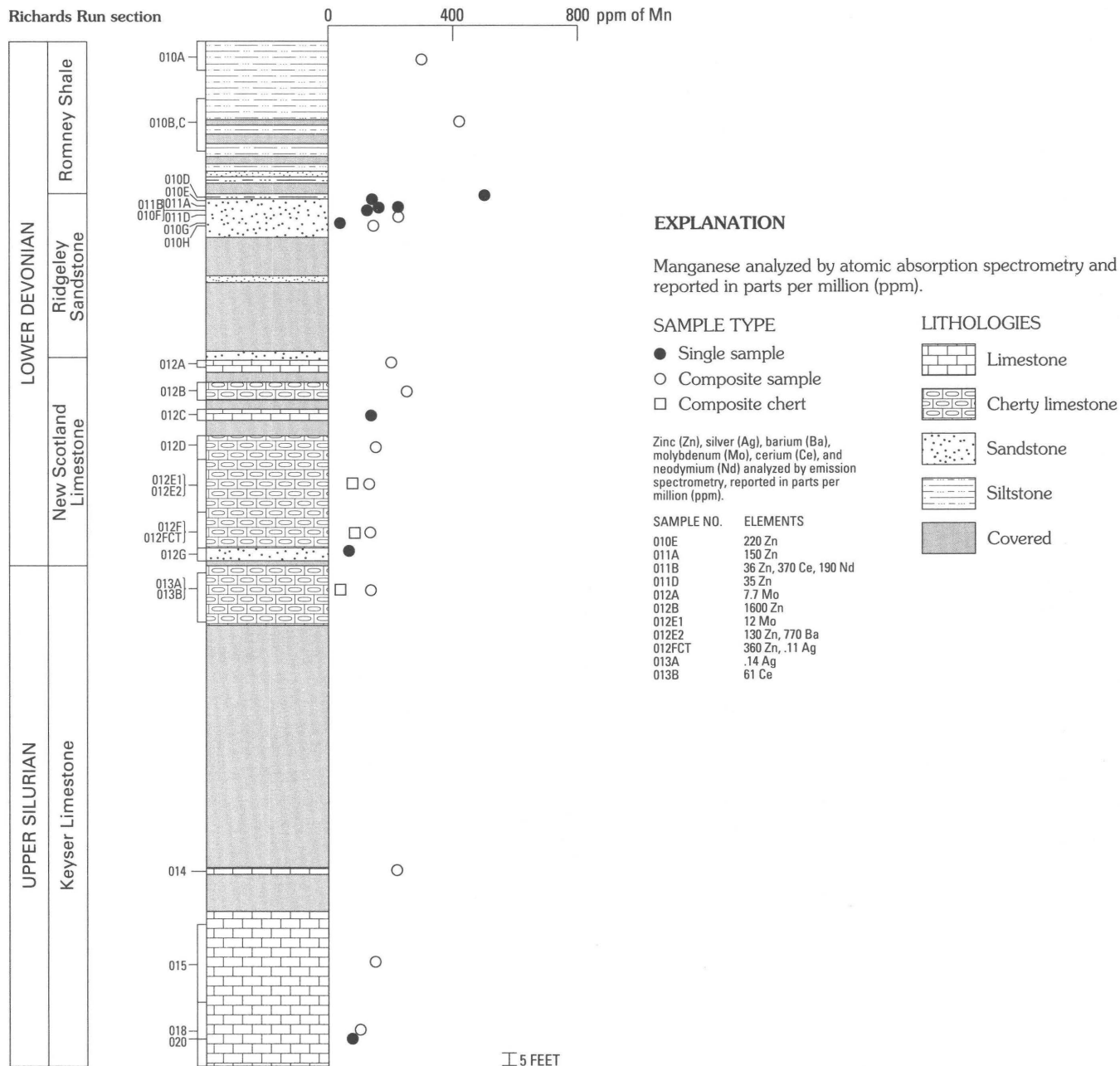


Figure 5C. Section at Richards Run.

of diagenetic chert and are instead siliceous because of their high silt-sized detrital grain contents. The detrital grains are mostly quartz with minor feldspar and detrital chert. Sample 053C (Fulks Run) has nearly 50 percent detrital grains (mostly quartz) and has 130 ppm of manganese. Sample 012B (Richards Run) has nearly 10 percent detrital grains (mostly quartz) and has 240 ppm of manganese. The high-silica limestones at Liberty Furnace (sample 032A) do contain diagenetic chert that has replaced part of its calcite cement. Sample 032A has the lowest manganese (96 ppm)

of the three limestones. The petrographic observations imply that manganese occurs in the carbonate phases of the New Scotland Limestone, most likely in the calcite cements rather than in detrital grains or chert.

No manganese phases were discovered during petrographic and SEM examination of the limestones. However, thin laminae of cement were observed to luminesce bright orange and yellow under the luminoscope in samples 012B and 032A. This is an indication of higher than normal manganese content and is evidence that the

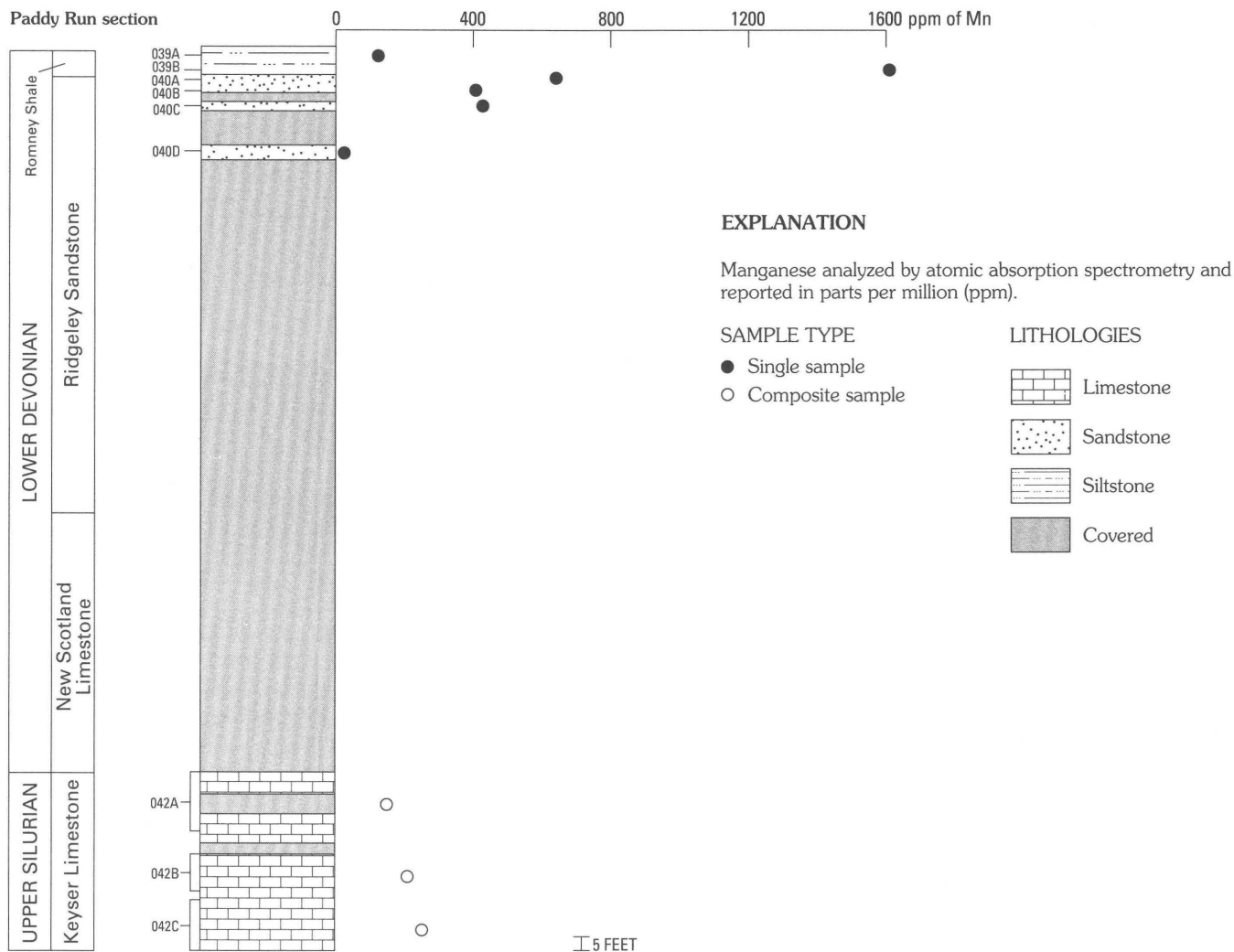


Figure 5D. Section at Paddy Run.

regional distribution of cathodoluminescent cement zones determined by Dorobek (1987) may extend at least beneath the Liberty Furnace and Richards Run areas (fig. 4).

The manganese contained in Romney Shale varies from 120 to 1,600 ppm of manganese.

The manganese contained in Ridgeley Sandstone varies from 8 to 640 ppm; where values exceed 400 ppm, the rock is obviously weathered.

The cherts collected from Fulks Run and Richards Run contained from 24 to 73 ppm of manganese. The cherts from Liberty Furnace contained from 100 to 1,500 ppm of manganese. The high manganese content of chert beds at Liberty Furnace are unusual, especially since these chert samples, unlike those collected from the other sections, contain more manganese than the adjacent samples of limestone.

## MANGANESE CONTENTS IN THE ROCKS OF THE LIBERTY FURNACE SECTION

### Field and chemical observations

A 300-ft-thick section of Ridgeley Sandstone and New Scotland Limestone was measured and collected less than 0.4 mi northeast of the Old Iron Furnace in the Liberty Furnace area of Virginia. Liberty Furnace lies between two ridge-top manganese prospects. The Gap Mountain Prospect is 2 mi to the west and the High Head Prospect is 3.5 mi to the northeast (fig. 2, localities *f* and *e*, respectively). Both prospects are at approximately 1,800 ft in elevation. At Liberty Furnace the Ridgeley Sandstone and New Scotland Limestone are exposed in a topographic gap occupied by Laurel Run at 1,300 ft in elevation. Exposures



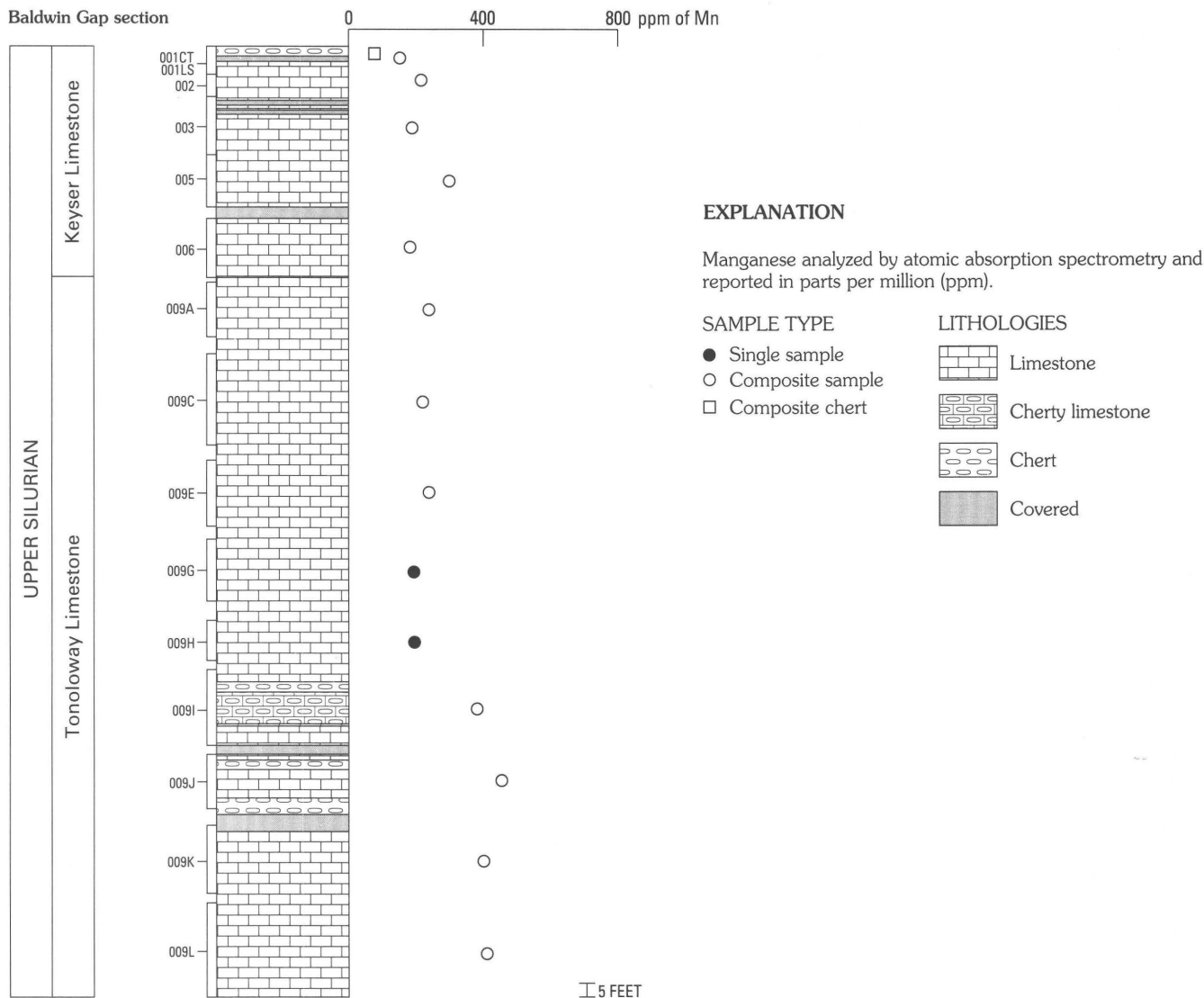


Figure 5E. Section at Baldwin Gap.

of the New Scotland Limestone are poor in other topographic gaps between the prospects.

A short section (approximately 300 ft) of the Ridgeley Sandstone and New Scotland Limestone beds exposed in Laurel Run (shaded area on fig. 6) are not shown on the geologic map of the Wolf Gap quadrangle (Young and Rader, 1974). The beds in Laurel Run strike north-south, (strikes range N13W to NS), dip steeply to the west (65–70°), and form the shared common limb of a local subsidiary syncline-anticline couplet that is situated on the tightly folded western limb of a large, regional, south-plunging syncline (fig. 6).

The section measured at Liberty Furnace consists of 150 ft of Ridgeley Sandstone (95 ft exposed) overlying 150 ft of New Scotland Limestone (110 ft exposed, fig. 5). The median manganese content for 13 sandstone samples is 40

ppm with most samples containing 18–62 ppm of manganese.

At the top of the measured Liberty Furnace section, the manganese content of 031A (fig. 5A) is less than the detection limit of the method of analyses (10 ppm), although the rock is pyritiferous and highly anomalous in phosphorous and rare earth elements (fig. 5A). The two sandstone samples collected stratigraphically below the sulfidic zone contain four times as much manganese (031B with 310 ppm and 031C with 260 ppm, fig. 5A) as the rest of the sandstone in the section. One explanation for the pattern observed here is that the local redistribution of manganese resulted in an enriched zone beneath a depleted zone.

There is a 33-ft covered interval between the last outcrop of Ridgeley Sandstone and the first outcrop of

**Table 1. Results of analyses of rock samples**

[The semiquantitative direct current arc emission spectrographic (S) method of analyses of silicon, aluminum, iron, magnesium, calcium, sodium, potassium, titanium, and phosphorus are reported in weight percent (%); the amounts of all other elements determined by the semiquantitative direct current arc emission spectrographic method are given in parts per million (ppm). Analyses of 84 samples were conducted by C. Skeen, U.S. Geological Survey Laboratories, Reston, Va.; analyses of 18 samples were conducted by C. Skeen and Z. Brown. The quantitative inductively coupled plasma (ICP) spectrographic analyses of iron are reported in weight percent (%); the amounts of manganese, barium, and phosphorous determined by ICP are given in ppm. Analyses of samples were conducted by W. d'Angelo, U.S. Geological Survey Laboratories, Reston, Va.

Symbols and abbreviations used in the table include: >, amount detected is greater than the upper limit of determination; <, amount detected is below the lowest limit of determination (which is the number preceding "<"); and —, not detected.

Of the 64 elements looked for spectrographically, 31 elements were mostly not found and have been omitted from the table. The omitted elements (with the detection limits in ppm following each element in parenthesis) are: arsenic (100), gold (6.8), bismuth (10), cadmium (32), dysprosium (22), erbium (4.6), europium (2.2), gadolinium (32), germanium (4.6), hafnium (15 and 150), holmium (6.8), indium (10), iridium (15), lithium (68), lutetium (15), osmium (15), palladium (1.0), praeosodymium (100), platinum (2.2), rhenium (10), rhodium (2.2), ruthenium (2.2), antimony (68), samarium (10), tantalum (320), terbium (32 and 46), thorium (46), thallium (10), thulium (4.6), uranium (220 and 460), and tungsten (15). Eight elements listed above were found as follows: sample 031A, 80 ppm dysprosium, 29 ppm erbium, 27 ppm europium, 21 ppm holmium, 150 ppm praeosodymium, and 51 ppm samarium; sample 032A, 55 ppm thorium; sample 031K, 31 dysprosium; sample 034, 230 ppm lithium; sample 035B, 53 ppm thorium; sample 035D, 71 ppm thorium; sample 039A with 3.4 ppm europium; and sample 011B, 19 samarium.]

Sample	Rock type	Si %-S	Al %-S	Mg %-S	Ca %-S	Na %-S	K %-S	Ti %-S	Ag PPM-S	B PPM-S
<b>Baldwin Gap</b>										
001CT	cherty limestone	>34.00	.15	.40	14	.07	.13	.007	<.10	8.0
001LS	limestone	9.50	.27	.65	>32	.04	.29	.011	<.10	<3.2
002	limestone	1.30	.20	.62	>32	.04	<.07	.020	<.10	<3.2
003	limestone	4.50	1.00	2.30	>32	.08	.36	.050	<.10	<3.2
005	limestone	1.60	.12	.55	>32	.04	.30	.017	<.10	<3.2
006	limestone	2.50	.28	.71	>32	.05	.26	.017	<.10	<3.2
009A	limestone	7.60	2.80	3.20	>32	.16	.77	.140	.13	17.0
009C	limestone	5.00	1.60	2.40	>32	.08	.51	.063	<.10	8.3
009E	limestone	6.10	1.90	3.00	>32	.07	.60	.078	.11	11.0
009G	limestone	7.90	2.40	1.80	>32	.11	.84	.140	.10	25.0
009H	limestone	7.10	3.00	2.30	>32	.14	.81	.110	.11	14.0
009I	cherty limestone	11.00	2.70	8.60	>32	.17	.79	.160	.13	21.0
009J	cherty limestone	13.00	2.20	2.30	>32	.20	.64	.110	.10	9.1
009K	limestone	7.90	2.60	2.80	>32	.20	.96	.200	.19	21.0
009L	limestone	8.80	2.20	2.50	>32	.19	.88	.160	.16	33.0
<b>Richards Run</b>										
010A	siltstone	31.00	16.00	2.20	2	.44	6.20	.610	.11	170.0
010BC	siltstone	30.00	17.00	2.20	1	.55	7.00	.440	.15	160.0
010D	claystone	31.00	16.00	1.70	1	.13	7.00	.490	.26	210.0
010E	argil-ss	>34.00	1.60	.15	0	.03	.35	.086	.15	51.0
010F	calc-ss	>34.00	.67	.06	3	.01	.08	.048	.11	13.0
011A	argil-ss	>34.00	2.20	.18	0	.03	.42	.100	.11	66.0
011B	calc-ss	>34.00	1.70	.13	2	<.01	.29	.067	<.10	34.0
011D	calc-ss	>34.00	.53	.05	2	.01	.08	.036	<.10	13.0
010G	sandstone	>34.00	.27	.03	0	<.01	<.07	.047	<.10	7.9
010H	sandstone	>34.00	.35	.03	0	.01	<.07	.040	.10	19.0
012A	limestone	7.50	.73	.61	>32	.07	.39	.027	<.10	<3.2
012B	cherty limestone	>34.00	.56	.27	12	.21	.19	.020	<.10	13.0
012C	limestone	4.00	.99	1.30	>32	.06	.42	.043	<.10	7.3
012D	cherty limestone	14.00	1.30	.76	>32	.06	.48	.049	<.10	11.0
012E1	cherty limestone	11.00	1.20	.57	>32	.10	.41	.050	<.10	12.0
012E2	chert	>34.00	.53	.14	1	.06	.11	.022	<.10	49.0
012FCT	chert	>34.00	1.10	.74	9	.09	.24	.038	.11	40.0
012F	cherty limestone	26.00	1.90	1.40	27	.17	.59	.076	<.10	29.0
012G	argil-calc-ss	>34.00	1.40	.29	3	.14	.41	.160	.13	23.0
013A	limestone	7.40	2.40	1.30	>32	.13	.76	.077	.14	21.0
013B	chert	>34.00	.41	.06	0	.05	.11	.020	<.10	75.0
014	limestone	10.00	4.30	2.10	>32	.09	1.40	.210	<.10	42.0
015	limestone	3.00	1.70	1.20	>32	.05	.56	.055	<.10	<3.2
018	limestone	1.80	.69	1.50	>32	.06	.39	.033	<.10	<3.2
020	limestone	12.00	.87	.54	>32	.05	.40	.035	<.10	5.5

**Table 1.** Results of analyses of rock samples—Continued

Sample	Rock type	Si %-S	Al %-S	Mg %-S	Ca %-S	Na %-S	K %-S	Ti %-S	Ag PPM-S	B PPM-S
<b>Liberty Furnace</b>										
031A	shaly limestone	17.00	3.20	.36	>32	.16	.84	.130	1.10	48.0
031B	sandstone	>34.00	.58	.05	0	.01	.12	.040	.14	20.0
031C	sandstone	>34.00	.62	.04	0	.01	.20	.036	<.10	24.0
031D	sandstone	>34.00	.64	.03	0	.01	.18	.043	<.10	16.0
031E	sandstone	>34.00	.86	.05	0	.02	.30	.065	<.10	32.0
031F	sandstone	>34.00	.69	.03	0	.01	.19	.060	<.10	26.0
031G	sandstone	>34.00	.58	.04	0	.02	.25	.049	<.10	24.0
031H	sandstone	>34.00	.24	.02	0	.01	.16	.017	<.10	9.4
031J	sandstone	>34.00	.11	.01	0	<.01	<.07	.017	<.10	14.0
031K	sandstone	>34.00	.41	.03	0	.01	.09	.031	<.10	22.0
031L	sandstone	>34.00	.41	.03	0	.01	.14	.030	<.10	16.0
031M	sandstone	>34.00	.37	.03	0	.01	.17	.034	<.10	19.0
031N	sandstone	>34.00	.53	.03	0	.01	.21	.039	<.10	18.0
031O	sandstone	>34.00	.45	.03	0	.03	.16	.052	<.10	19.0
035A	cherty limestone	>34.00	2.50	.39	18	.45	.84	.100	.13	34.0
035A2	cherty limestone	13.00	5.30	2.70	>32	.09	2.20	.250	<.10	59.0
035B	cherty limestone	>34.00	2.40	.48	22	.42	.82	.089	.17	41.0
035C	argil-calc-ss	>34.00	2.40	.33	11	.55	1.20	.150	.16	45.0
035C86	argil-ss	>34.00	1.90	.09	0	.02	.62	.250	.20	82.0
035D	cherty limestone	30.00	2.10	.50	29	.23	.82	.130	.25	27.0
035E	cherty limestone	>34.00	1.90	.46	25	.25	.72	.120	<.10	46.0
032A	cherty limestone	>34.00	2.10	.50	21	.18	.67	.140	.14	66.0
032B	cherty limestone	12.00	.71	.38	28	.02	.34	.034	<.10	8.5
032BCT	chert	>34.00	.42	.13	5	.01	.11	.018	<.10	34.0
032B2C	chert	>34.00	.46	.06	0	.01	.14	.023	<.10	36.0
032C	chert	>34.00	.33	.05	0	.01	.12	.016	.11	41.0
032C6	chert	>34.00	.67	.07	0	.01	.15	.028	.12	66.0
032C10	chert	>34.00	.68	.07	0	.02	.16	.051	<.10	61.0
032CT	chert	>34.00	1.00	.13	0	.01	.20	.041	.16	82.0
034	shaly limestone	16.00	5.20	1.60	16	.05	1.70	.250	<.10	79.0
<b>Paddy Run</b>										
039A	siltstone	26.00	14.00	1.10	0	.09	4.50	.290	<.10	190.0
039B	siltstone	23.00	12.00	.75	0	.12	6.00	.470	.37	170.0
040A	sandstone	22.00	.88	.05	1	.10	<.07	.093	.65	16.0
040B	sandstone	>34.00	.40	.02	1	.01	<.07	.032	<.10	7.2
040C	sandstone	>34.00	.17	.02	0	<.01	<.07	.026	<.10	5.8
040D	sandstone	>34.00	.08	.01	0	<.01	<.07	.010	<.10	<3.2
042A	limestone	3.50	2.50	1.60	>32	.06	.77	.083	<.10	5.3
042B	limestone	3.90	1.50	2.10	>32	.06	.51	.061	<.10	<3.2
042C	limestone	8.90	3.30	1.60	>32	.14	1.40	.180	<.10	28.0
<b>High Head Prospects</b>										
045A	limestone	2.20	.08	.44	>32	.02	.27	.008	<.10	<3.2
045B	cherty limestone	23.00	2.20	.67	18	.12	.84	.100	<.10	23.0
045C	limestone	8.10	2.70	1.50	>32	.13	1.10	.140	<.10	25.0
<b>Fulks Run</b>										
050A	sandstone	>34.00	.56	.03	0	.03	.16	.031	<.10	7.2
050B	sandstone	>34.00	.66	.03	0	.01	.17	.045	<.10	19.0
050C	sandstone	>34.00	.78	.03	0	.06	.30	.037	.11	11.0
959D	sandstone	>34.00	1.40	.06	0	.10	.56	.053	<.10	28.0
050E	sandstone	>34.00	1.10	.04	0	.10	.30	.150	<.10	46.0
050F	sandstone	>34.00	1.50	.07	0	.31	.55	.130	<.10	58.0
050G	sandstone	>34.00	3.00	.15	0	.43	.83	.220	.10	65.0
050H	sandstone	>34.00	1.80	.14	0	.01	.49	.360	.18	120.0
050IS	sandstone	>34.00	1.80	.12	0	.01	.31	.260	.19	83.0

**Table 1.** Results of analyses of rock samples—Continued

Sample	Rock type	Si %-S	Al %-S	Mg %-S	Ca %-S	Na %-S	K %-S	Ti %-S	Ag PPM-S	B PPM-S
<b>Fulks Run—Continued</b>										
050IC	chert	>34.00	.26	.01	0	.01	<.07	.008	<.10	48.0
050J	chert	>34.00	.22	.02	0	.01	<.07	.009	<.10	62.0
053A	cherty limestone	26.00	1.80	.41	10	.34	.75	.092	<.10	20.0
053B	cherty limestone	23.00	1.60	.41	15	.25	.55	.059	.12	19.0
053C	cherty limestone	22.00	1.20	.39	18	.19	.41	.076	<.10	45.0
055A	limestone	1.90	1.20	1.10	>32	.04	.57	.038	<.10	<3.2
055B	shaly limestone	16.00	4.10	1.60	16	.08	2.60	.170	<.10	95.0
055C	limestone	1.40	.06	.51	>32	.03	.24	<.003	<.10	<3.2
055D	shaly limestone	12.00	3.00	1.30	>32	.13	.91	.130	<.10	16.0
<b>Bonnet Hill</b>										
060A	limestone	.47	.13	.48	>32	.03	.30	.013	<.10	<3.2
060B	sandstone	>34.00	.17	.01	0	<.01	<.07	.020	<.10	<3.2

limestone of the New Scotland Limestone. The limestones are dark gray and interbedded with chert bands of variable width. The limestones are composed of approximately 10–40 percent sand-sized detrital grains (mostly quartz) in a matrix of micritic carbonate mud. The manganese contents of the limestones steadily decrease from 240 ppm at the top to 90 ppm near the bottom of the section (those beds above the massive chert beds) as the limestones become increasingly cherty (fig. 5). The chert bands are parallel to bedding in the limestone and vary from stringers of black chert fragments to beds of irregular knots (generally 6 in across) of mostly black chert at the top of the section to 5-ft-thick beds of massive grayish-white to bluish-black chert at the base of the section.

The highest manganese contents (650–1,500 ppm) in the Liberty Furnace section were found in four samples of chert in the lowermost 30 ft of the New Scotland Limestone (fig. 5). Three of the six chert samples contain 1,200–1,500 ppm of manganese (fig. 5). The concentration of manganese here is in part attributed to the axial position of the cherts in the syncline and the circulation of ground water through the fractures associated with the tight synclinal folding.

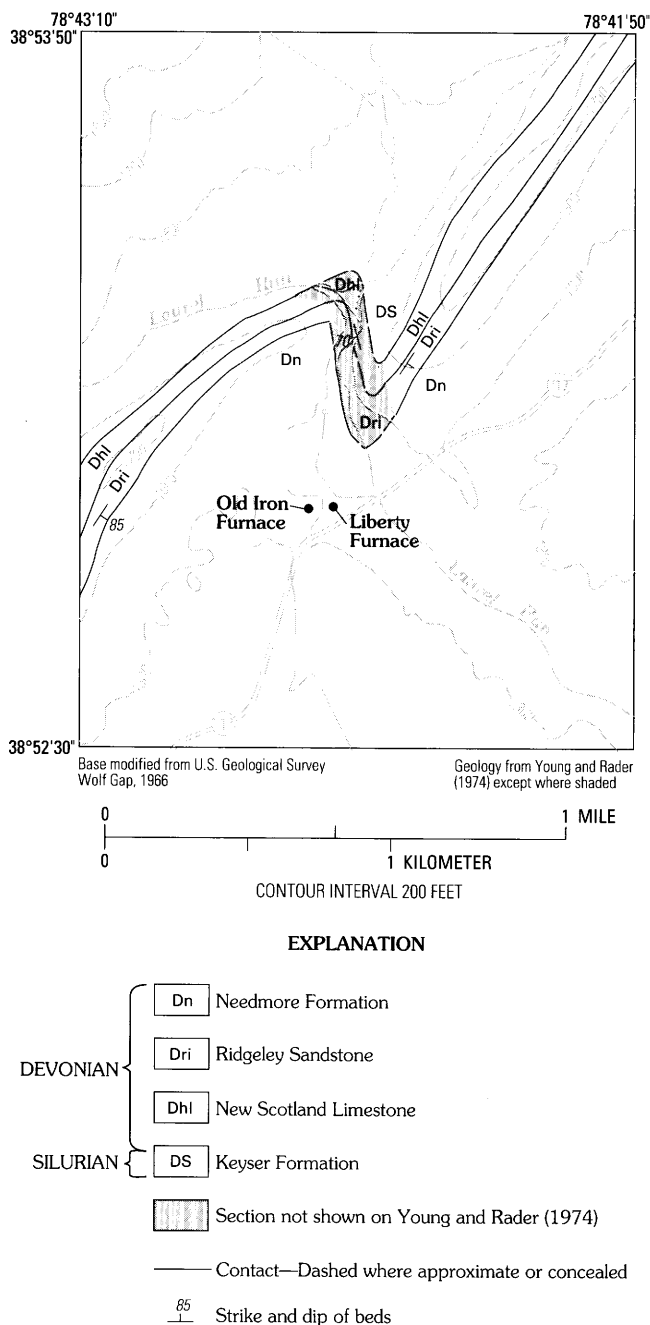
### Petrographic observations

Several grains of hematite were identified in chert from Liberty Furnace (sample 032C, fig. 5A), but no manganese phases were observed in the hematite or in the other grains examined petrographically and with the SEM. The distribution of the unidentified manganese phase may be analogous to the distribution of the hematite. Hematite (at most, 0.54 weight percent) is generally clustered in one region, which takes up less than a thousandth of the area seen in thin section. Manganese may be present in these cherts as a discrete, heterogeneously disseminated phase that escaped intersection by the thin section. One can

assume that the chance of missing phases of such small concentration and uneven distribution in thin section is great.

Redistribution of manganese in carbonate cements may have been facilitated by rock porosity and permeability created by pressure-dissolution and tectonic fractures. Some of the features (observed in thin section) that give information on the changes in porosity and permeability of the rocks since early diagenesis include:

1. Oxidized minerals. Spherical pyrite framboids are found interstitial to quartz grains in sample 032A (fig. 5A). The framboids grew in a reducing environment, which is also suitable for manganese concentration. Many of the smallest framboids are replaced by hematite. Replacement apparently proceeded from the outer rims inward, as the largest framboids have only a few hematite cells on the outermost rim. Replacement of pyrite occurred while the limestone was permeable to oxidizing (fresh) water, otherwise the interiors of the largest framboids would also be oxidized. Fresh water may remove and redistribute manganese, thus the low manganese level (96 ppm) in sample 032A.
2. Crushed grains. Dissolution of original carbonate material by fresh water is implied where there are crushed marine ooids, ooid molds filled with calcite cement, and secondary calcite growths on grains (Bathurst, 1986). All three are seen in sample 032A.
3. Stylolites. Dissolution of original material is evident where stylolites cross the chert (sample 032C, fig. 5A). The stylolites enclose bands of insoluble (noncarbonate) residues that were concentrated upon removal of original material.
4. Silicified fragments. Dissolution of original carbonate material is evident where chert replaces echinoderm ossicles in the cherty limestone and chert near basal New Scotland Limestone (samples 032A and 032C, fig. 5A). In contrast, the bioclastic fragments in the limestones at



**Figure 6.** Outcrop map of the Ridgeley Sandstone and New Scotland Limestone near Liberty Furnace, Va.

Fulks Run and Richards Run appear to be original material. The silicified fossils indicate that the massive chert beds were at one time limestone beds.

5. Tectonic fractures. Permeability was enhanced by more than one generation of fractures. In the chert (sample 032C, fig. 5A), fractures are filled with mosaic quartz and are cross-cut by diffusely bounded channels of dirty amorphous chert. Hairline fractures with minor offsets bisect silicified echinoderm ossicles, indicating that the

silicification preceded later deformation. Repeated tectonic fracturing increased the opportunity for the passage of ore-scavenging or ore-bearing solutions.

## DISCUSSION

Fresh samples of limestone and sandstone hosts and parents to supergene manganese deposits generally contain from 100 to 400 ppm of manganese. The manganese is thought to be locally concentrated in thin laminae of the calcite cement (primary). Limestone beds in which silica has pervasively replaced calcite and in which permeability has been enhanced by tectonic fracturing are slightly enriched in manganese (650–1,500 ppm). The manganese is thought to occur as discrete, heterogeneously disseminated oxide phases (secondary).

The composition of the calcite cement and local rock permeability may be the major factors in residual concentration of manganese. As manganiferous cement was dissolved by pressure-dissolution or in the process of silicification, the manganese ions remained in place as insoluble residues. Late Paleozoic deformation and subsequent erosion brought the beds to the surface where weathering of the carbonate left insoluble chert, sandy clay, and manganese or iron oxides in place of the original beds. Tectonic fractures enhanced the permeability of the cherts, which at times increased their favorability as hosts for manganese concentrations.

## HYPOTHESIS OF MANGANESE ENRICHMENT

There are zones of brightly luminescent-highly manganiferous cements in limestones of the upper Helderberg Group, that were deposited near the eastern shore of the Devonian Appalachian basin (Dorobek, 1987). Dorobek (1987) suggests that these zones are fixed and limited in geographic distribution by the distances meteoric ground waters traveled from the recharge areas exposed in Devonian time. Accordingly, reconstruction of the basin geometry and the location of the recharge areas should enable one to locate the zones of manganese-rich carbonate cement.

The author suspects there is a correlation between the location of supergene manganese deposits and the paleo-zone corresponding to the limit of travel of the reduced meteoric ground water. Further study should be made to confirm that the supergene manganese deposits in this study area are underlain by zones of manganese-rich carbonate-cement.

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