# Barite Nodules in Devonian Shale and Mudstone of Western Virginia

## U.S. GEOLOGICAL SURVEY BULLETIN 1880

U.S. DEPARTMENT OF THE INTERIOR
March 3, 1849

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# Barite Nodules in Devonian Shale and Mudstone of Western Virginia

## By SANDRA H.B. CLARK and ELWIN L. MOSIER

A proposed origin of barite nodules in Devonian shale and mudstone of the Appalachian basin in western Virginia based on physical characteristics of the nodules and on the stratigraphy, paleoenvironment, and geochemistry of the shale and mudstone

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MANUEL LUJAN, Jr., Secretary

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# Barite Nodules in Devonian Shale and Mudstone of Western Virginia

*By* Sandra H.B. Clark *and* Elwin L. Mosier

## Abstract

Barite nodules are present in the Devonian Needmore Shale and in calcareous members of the overlying Millboro Shale at several localities in western Virginia. The barite nodules are diagenetic features that formed in shale and mudstone that were deposited slowly in oxygen-deficient marine environments.

The shale or mudstone matrix of the barite nodule zones is enriched in manganese, cobalt, nickel, and zinc compared to shale or mudstone that is not near barite nodule localities. In a locality near Boiling Spring, for example, light-colored mudstone deposited in a dysaerobic environment contains barite nodules. Mudstones from the dysaerobic zone and an overlying aerobic zone are slightly enriched in manganese, cobalt, nickel, and zinc. Overlying and underlying dark-gray shales from anaerobic zones are slightly depleted of these elements. On the other hand, the barite nodule zones are depleted in silver and lead, but areas away from these zones show enrichment in these elements.

Physical characteristics of the nodules and stratigraphy, paleoenvironment, and geochemistry of the associated shale and mudstone suggest that barite precipitated at interfaces between anaerobic and dysaerobic water and in the vicinity of the formation of calcareous lenses and concretions that formed in anaerobic to dysaerobic environments. A model for precipitation of barite derived from dilute, diverse sources at interfaces of anoxic water with more oxygenated waters is suggested as a feasible alternative to models requiring barium be derived from springs or other kinds of hydrothermal fluids. Barium that is introduced into seawater from dilute, diverse sources can be concentrated as authigenic marine barite or in marine organisms, can later be dissolved in anoxic water, and then can be precipitated at interfaces with more oxygenated waters. The existence of concentration gradients may account for the migration of barium toward the interface in production of barite nodules. Geologic relations of the barite nodules suggest that the boundary between anaerobic and dysaerobic pore water below the sediment-water interface served as a locus for the formation of barite nodules. Sulfur-reducing bacteria may have served as a catalyst. Barite that formed in association with carbonate concretions and lenses in aerobic to dysaerobic environments may have precipitated in areas of locally increased pH associated with decaying organic matter.

## INTRODUCTION

Barite nodules occur in Devonian shale and mudstone at many localities in the Appalachian basin (Lesure, 1957; de Witt, 1974; Dennison and others, 1979; Way and Smith, 1983; Clark, 1985, 1986a,b, 1987; Pepper and others, 1985; Nuelle and Shelton, 1986). The word "nodule" is used in this paper as a general term that includes rosettes, which have radiating structure, and concretions, which have concentric structure. In the past, the occurrences have been of interest primarily as mineralogical curiosities. Recently, the occurrences of barite nodules in shale have provoked interest because their geologic setting is similar to that of large, commercial bedded barite deposits and because barite is commonly associated with large sedimentary exhalative base-metal deposits (Brobst, 1984).

The objectives of this study were to locate and describe the barite occurrences in shale and mudstone of western Virginia and to find out whether the geochemistry of the shale and mudstone, together with the physical features of the nodules and enclosing rocks, would help determine if the nodules had been formed by submarine spring activity in the area or if they had originated in some other way. This report describes the barite nodules, presents the results of chemical analyses of the enclosing shales, and describes the depositional environments in which the barite nodules formed. The report evaluates the features of the nodules and enclosing rocks and suggests a feasible model for the origin of the observed features.

## LOCATION AND DESCRIPTION OF BARITE OCCURRENCES

Barite nodules are found in the Lower to Middle Devonian Needmore Shale of the Clifton Forge and

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**Table 1.** Occurrences of barite nodules in Devonian shale and mudstone in western Virginia

| Locality name | Locality number | 7.5-minute quadrangle | Latitude and longitude | Host rock | Remarks |
|---|---|---|---|---|---|
| **Clifton Forge area** | | | | | |
| Hickory Hill | 1 | Jordan Mines | 37°41′20″<br>80°06′35″ | Needmore Shale | Barite nodules from poorly exposed shales, which are locally fossiliferous. |
| Doctors Ridge | 2 | Alleghany | 37°40′03″<br>80°08′15″ | do. | Barite nodules from poorly exposed shale. |
| Boiling Spring | 3 | Jordan Mines | 37°41′00″<br>80°05′18″ | Millboro Shale | Excellent exposures in roadcut. Barite nodules and calcareous concretions in calcareous shale. Fossils locally in section. |
| Pike Pond | 4 | Clifton Forge | 37°52′02″<br>79°47′50″ | do. | Barite in veinlets in calcareous concretions and nodules overlying concretion zone. Good exposures; accessibility poor. |
| Strom | 5 | Strom | 37°42′45″<br>79°53′40″ | Millboro Shale(?) | Single weathered barite nodule found beside road; shale in roadcut. |
| Oriskany | 6 | Oriskany | 37°36′50″<br>79°59′20″ | Millboro Shale | Barite nodules in zone of calcareous concretions (location approximate). |
| **Williamsville area** | | | | | |
| Williamsville | 7 | Williamsville | 38°11′45″<br>79°34′05″ | Needmore Shale | Abundant barite nodules in shale exposures and ditch at roadside. |
| Flood | 8 | do. | 38°14′18″<br>79°35′00″ | Millboro Shale | Barite veinlets in calcareous and pyritic concretions in roadcuts. |
| McDowell | 9 | Monterey SE. | 38°18′03″<br>79°31′05″ | do. | Barite in nodules and as veinlets in calcareous concretions in roadcuts. |
| **Mason Cove, Radford, and Mountain Lake areas** | | | | | |
| Mason Cove | 10 | Salem | 37°22′18″<br>80°03′34″ | Millboro Shale | Barite in small nodules and filling fractures in calcareous concretions. |
| Radford | 11a | Radford N. | 37°07′41″<br>80°30′35″ | do. | Do. |
| | 11b | do. | 37°07′47″<br>80°29′44″ | do. | Do. |
| Little Stony Creek | 12 | Interior | 37°23′24″<br>80°34′07″ | Millboro Shale(?) | Coarse-grained barite in float. |

Williamsville areas of west-central Virginia (table 1; figs. 1 and 2). Additionally, in the vicinities of Clifton Forge, Mason Cove, Radford, and Mountain Lake, Va., barite nodules occur in the Middle to Upper Devonian Millboro Shale but are generally in or adjacent to intervals containing calcareous lenses or concretions. Barite also is present within fractures in these lenses and concretions. Field work was conducted at all of the localities, and descriptions are given below. Chemical analyses were performed on representative samples of shale and mudstone collected from regularly spaced intervals of uniform lithology. Shale and mudstone from the beds in which barite nodules occur (referred to as barite matrix shales) were sampled at several localities and compared with samples from other localities where the shale and mudstone did not contain barite nodules.

## Clifton Forge Area

Barite nodules occur in the Needmore and Millboro Shales at three localities near the town of Boiling Spring (Hickory Hill, Doctors Ridge, and Boiling Spring localities), south of Pike Pond near the town of Clifton Forge, and near the towns of Strom and Oriskany (Lesure, 1957; Nuelle and Shelton, 1986). Rocks containing barite nodules are exposed at Hickory Hill (locality 1, table 1, fig. 1) in low banks along Virginia State Route 613 about 2 mi northwest of its intersection with Route 18 at Boiling Spring. At the Hickory Hill locality, barite nodules occur in the Needmore Shale in three layers of mudstone contained in a zone about 10 m thick that lies 10 to 20 m above the contact with the Oriskany Sandstone. In some layers, barite nodules compose 2 to 4 percent (by volume) of the rock. In the lowest of the three layers, the nodules are subrounded, irregular forms that are from 2 to 6 cm in diameter and are composed of equigranular black barite in a clay matrix. Barite nodules higher in the section are commonly rosettes of thin, radiating, bladed barite with interstitial clay. Many of the rosettes are hollow and have a geode-like form in which coarse, crystalline barite surrounds a central cavity (fig. 3). The rosettes are typically 3 to 4 cm in diameter and spherical in shape and have a rough surface. Some nodules

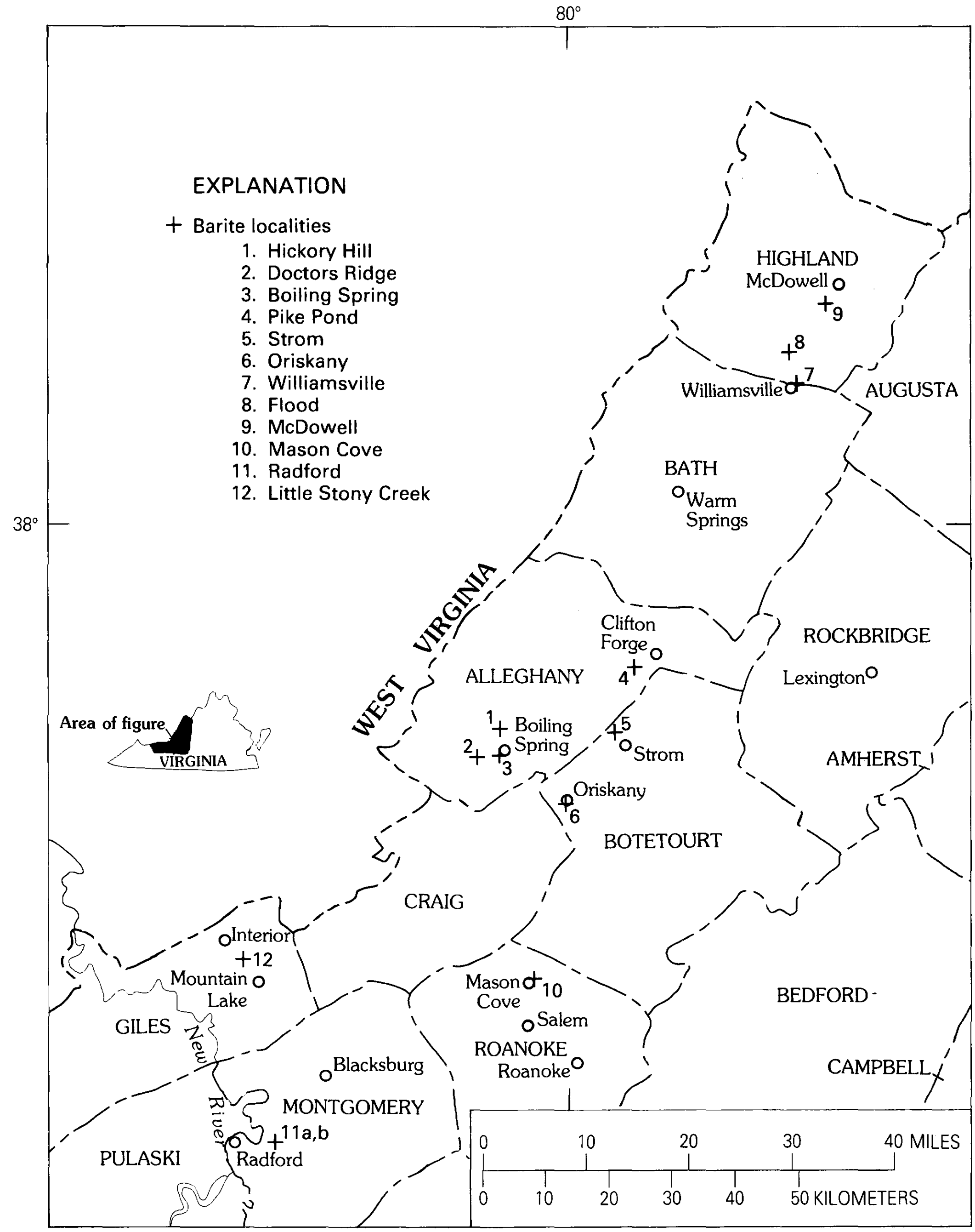

Figure 1. Locations of barite nodule occurrences.

are oblate spheroids or coalesced rosettes that have subrounded, irregular shapes.

The shale below the barite nodule zone on Hickory Hill is dark gray to grayish black, commonly carbonaceous, and fissile. Except for rare inarticulate brachiopods, the shale is unfossiliferous. In and above the barite nodule zone are light- to medium-gray, olive-gray, or yellowish-gray nonfissile mudstones that contain sparse pelagic fossils and evidence of bioturbation. These fossils were identified by J.T. Dutro, Jr. (U.S. Geological Survey), as *Styliolina fissurella* (Hall), *Tentaculites* cf. *T. bellulus* Hall, and *Buchiola halli* Clarke. About 3 to 4 m above the barite zone is a coquina composed almost entirely of tiny shells of the brachiopod *Ambocoelia virginiana* Prosser. This shell bed is overlain by silty, light- to medium-gray and olive-gray nonfissile shale containing abundant fossils, including sev-

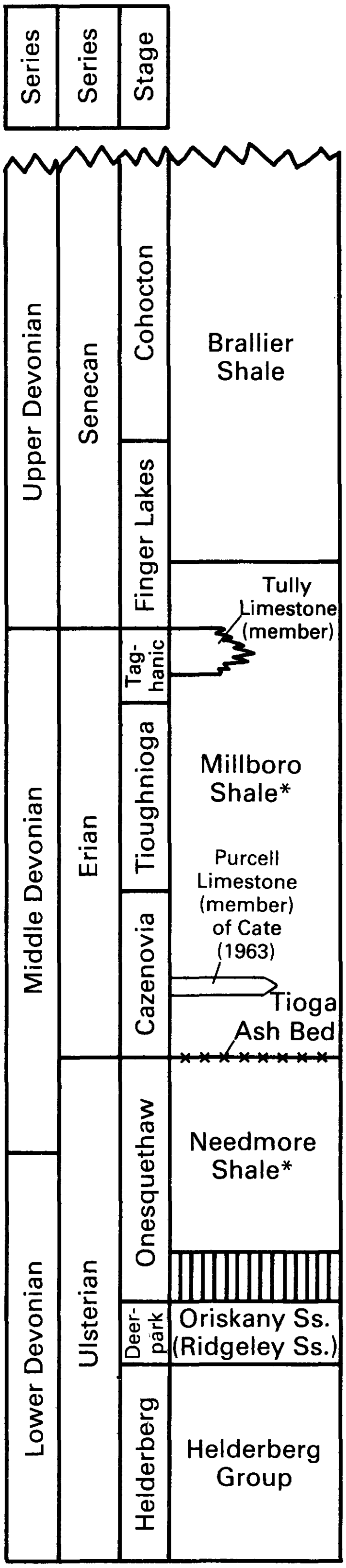

**Figure 2.** Stratigraphic column showing Devonian units in western Virginia that contain barite nodules (indicated by asterisks). Adapted from Oliver and others (1968, 1969). Vertical line pattern indicates hiatus.

eral kinds of brachiopods, ostracods, and styliolinids, from which J.T. Dutro, Jr., identified the following: *Cupularostrum limitare* (Vanuxem), *Styliolina fissurella* (Hall), *Chonetes* sp., *Tentaculites* sp., and an undetermined species of rhynchonelloid brachiopod. A *Phacops* trilobite was also found in this portion of the section.

Weathered barite nodules also occur on Doctors Ridge (locality 2, table 1, fig. 1) near a small cemetery located on a dirt road on the north side of the Sampson Branch of Potts Creek. The nodules are generally oblate or discoidal and measure 2 to 3 cm on the long axis. They contain equigranular, black barite grains in a clay matrix. Outcrops of Needmore Shale near the occurrences of barite nodules are meagre but are characterized by both black carbonaceous shale and brownish-gray silty shale containing abundant molds of brachiopod shells. The barite nodule locality is very near the contact of the Oriskany Sandstone with the overlying Needmore Shale (Lesure, 1957). The Doctors Ridge zone is probably an extension of the barite nodule zone on Hickory Hill, on the basis of its stratigraphic position and the projected trend of bedding.

Barite nodules in a roadcut of Virginia State Route 18 about 0.9 mi southwest of Boiling Spring (locality 3, table 1, fig. 1) are in a calcitic zone within the Millboro Shale (Dennison, 1961). Barite nodules, which make up 3 to 4 volume percent of some beds, are generally rosettes about 3 cm in diameter. Some rosettes are coalesced and locally form lenticular aggregates composed of numerous small, coalesced rosettes. The barite nodules occur in and above beds containing calcareous nodules and concretions that are about 30 cm long (fig. 4). Small pyritic nodules and concretions about 1 cm in diameter occur in calcareous mudstones below and in the lower part of the zone of baritic and calcareous nodules and concretions. Laminae in the enclosing rocks curve conformably around the baritic and pyritic nodules and the calcitic nodules and concretions (fig. 5). Brachiopod fossils occur in the calcareous shale underlying the baritic and pyritic nodule-bearing beds, but only bioturbation was found in the calcareous shales that contain baritic and pyritic nodules. The barite nodule zone is overlain by gray calcareous mudstone and argillaceous limestone.

Barite occurs in a calcitic zone of the Millboro Shale in a steep bank south of Pike Pond (locality 4, table 1, fig. 1) (Nuelle and Shelton, 1986). The outcrop contains septarian calcareous concretions and nodules that have calcite, dolomite, and barite in veinlets filling shrinkage fractures. Barite nodules occur in the gray to black shales overlying the zone of calcareous nodules and concretions. No body fossils have been found, but evidence of burrows is present in the shales that make up the calcareous nodule and concretion zone (Nuelle and Shelton, 1986).

A single barite nodule was found next to outcrops of Millboro(?) Shale along Virginia State Route 621 about 2 mi north of Strom (locality 5, table 1, fig. 1). The nodule

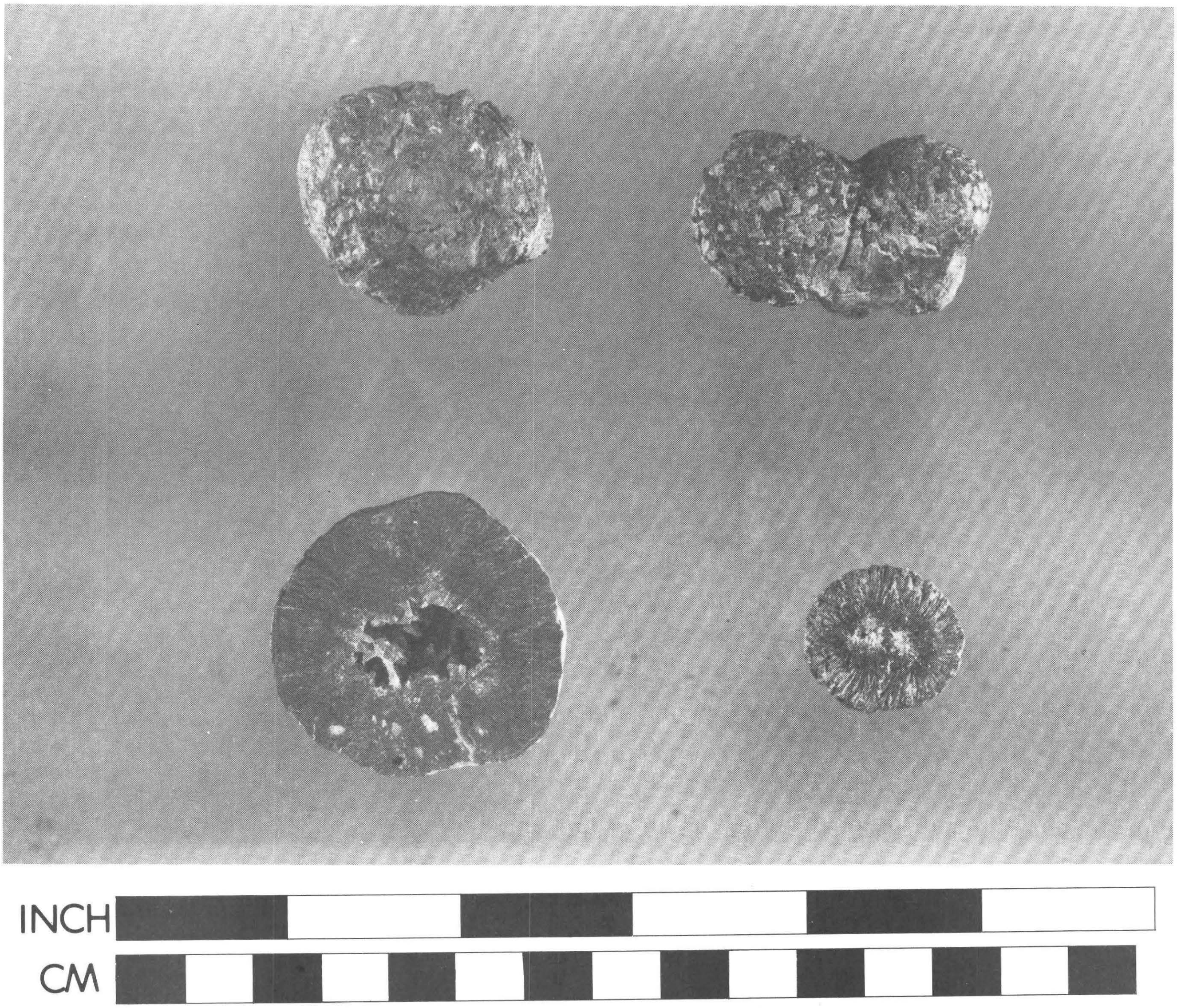

**Figure 3.** Barite nodules from Hickory Hill (locality 1).

consists of radially bladed barite surrounding a central cavity lined with barite crystals. The shales exposed in the area are predominantly unfossiliferous and black to dark gray in color. Yellowish-gray mudstone containing styliolinids and tentaculitids is exposed a few tens of meters above the barite occurrence.

Lesure (1957) found small barite nodules locally in the upper part of the Millboro Shale in Craig Creek valley near the town of Oriskany, Va. (locality 6, table 1, fig. 1). The barite nodules were in a zone of large calcareous concretions that grades laterally into a zone of thick-bedded argillaceous limestone.

## Williamsville Area

Barite occurs as nodules in exposures of shale in a roadcut on Virginia State Route 614 at a curve just beyond the bridge that crosses the Bullpasture River, northeast of the town of Williamsville (locality 7, table 1, fig. 1). The nodules are in the lower part of the Millboro Shale near its contact with the Oriskany Sandstone, as mapped by Bick (1962). Bick did not differentiate the Needmore Shale from the Millboro Shale, but the stratigraphic position and features of the shale in outcrops at the barite locality are those of the Needmore Shale.

The barite nodules are present immediately below a zone of fossiliferous, calcareous, medium-gray shale and mudstone that overlies fissile, dark-gray, locally pyritic calcareous shale. The fossils are very small brachiopods (*Ambocoelia*), *Tentaculites*, and *Styliolina*. The nodules constitute about 5 percent by volume of the shale layers in which they occur and have a wide variety of forms, the most common being rosettes or coalesced rosettes of thin, radially bladed barite with interstitial clay. Coarser crystalline

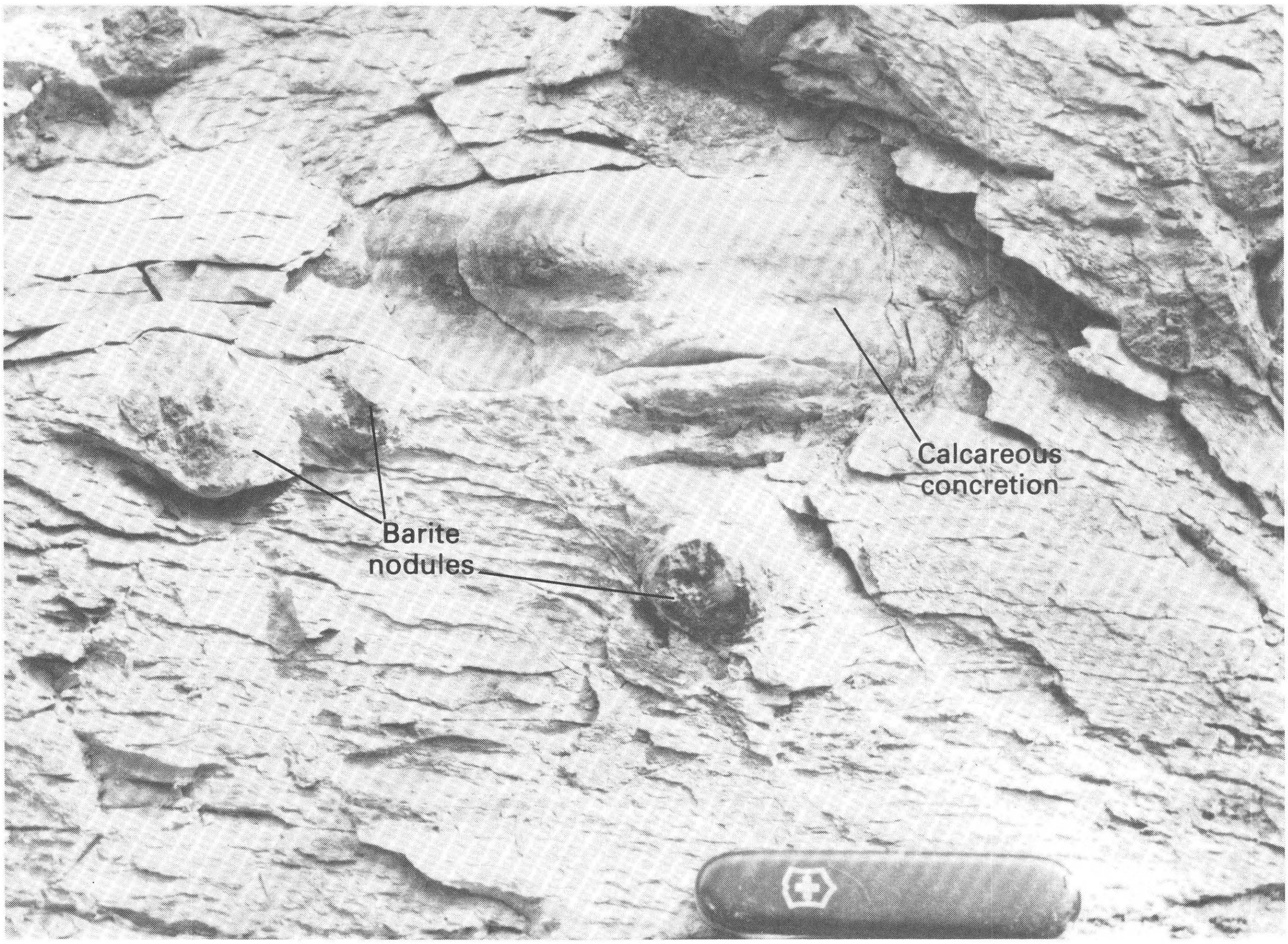

**Figure 4.** Barite nodules and calcareous concretion in the Millboro Shale near Boiling Spring (locality 3).

barite fills the central portion or surrounds central cavities, some of which are filled with clay. The nodules are mostly spherical or oblate and range in diameter from less than 1 to more than 12 cm; most commonly they are 3 to 4 cm in diameter. In one large, oblate nodule (9 cm on the long axis), coarse-grained calcite crystals surround a fine-grained calcareous core. The coarse crystals are in turn surrounded by fine-grained, finely banded colloform barite (fig. 6*A*). In some nodules, a fine-grained, calcareous core is surrounded by coarsely crystalline barite, itself surrounded by a calcareous layer and then a layer of fine-grained, dark-gray barite (fig. 6*B*). Part of a large, hollow barite nodule is composed of dark-gray, radially bladed barite that has small, mound-like projections of radiating barite blades on the inner surface (fig. 6*C*). Barite crystals fill open spaces between the inner surface and the fibrous, radiating barite that forms the outer portion of the shell.

Barite also occurs in veinlets filling fractures in calcareous concretions in the Millboro Shale near the intersection of Virginia State Routes 609 and 678, about 0.5 mi east of Flood (locality 8, table 1, fig. 1) and in a roadcut by the Bullpasture River on Virginia State Route 678, 3.7 mi south of McDowell (locality 9, table 1, fig. 1). In both localities, large (40 to 70 cm on the long axis) calcareous concretions, some of which are septaria, occur in strongly sheared, dark-gray shale, calcareous shale, and shaly limestone. The veinlets in the concretions are predominantly calcite, locally accompanied by barite and sphalerite.

Pyritic concretions, some having shrinkage fractures filled by barite, are present at both sites but are especially well developed at locality 8 (fig. 7). Although barite does not occur as discrete nodules at locality 8, as at the other localities described, this locality is included because of the similarity in geologic setting to the other localities in the Millboro Shale and because of the occurrence of barite within pyrite nodules.

Equigranular baritic nodules occur south of McDowell (locality 9, table 1, fig. 1) but are rare. Baritic, calcitic, and pyritic nodules are in dark-gray to black shale that

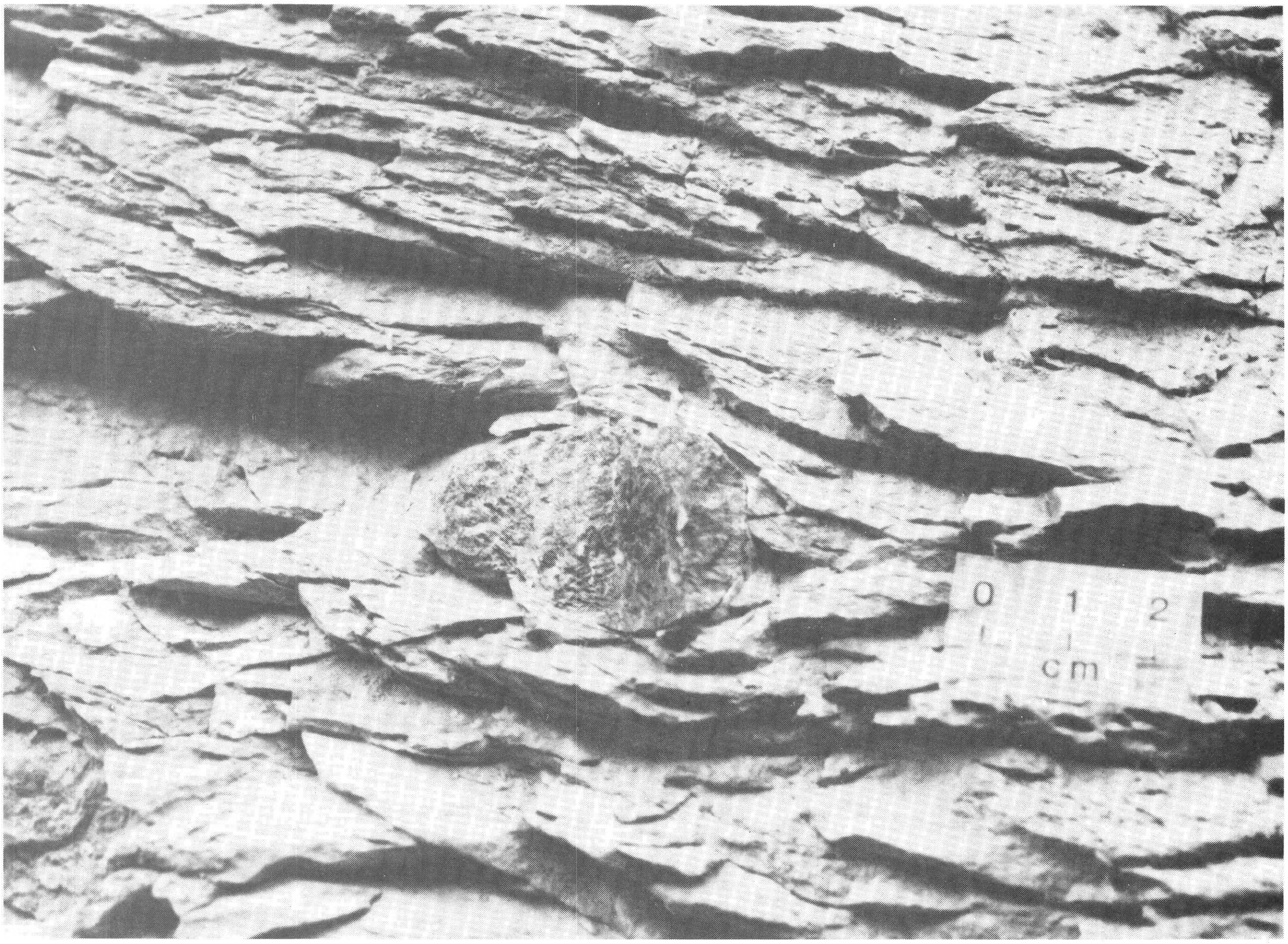

**Figure 5.** Barite nodule from near Boiling Spring (locality 3) showing curved laminae of enclosing rocks.

contains interbedded calcareous and shaly limestone layers, some of which are fossiliferous (bivalves). The shale is generally fissile, contains some pyritic and carbonaceous layers, and is intensely sheared in some layers. Trace fossils are preserved locally in the shale in the zones containing calcareous concretions but not in the zones containing pyritic nodules.

Similar occurrences of calcareous concretions have been noted at many other localities in western Virginia and West Virginia. Both barite and sphalerite locally accompany calcite as fracture fillings in the concretions.

## Mason Cove, Radford, and Mountain Lake Areas

In a quarry near Mason Cove, beside Virginia State Route 311 north of Salem and Roanoke (locality 10, table 1, fig. 1), barite occurs as small nodules (1 to 2 cm in diameter) and also fills fractures in calcareous concretions in the Millboro Shale near its contact with the overlying Brallier Shale, as mapped by Woodward (1932). The barite filling some of the fractures occurs as large (approximately 12 cm in the long dimension), radiating aggregates of bladed crystals (fig. 8). Pyrite is locally abundant in the shales and in the calcareous nodules, where it generally appears as concentric layers at the rims. The enclosing shales are intensely sheared in some zones and have a carbonaceous appearance.

Barite nodules are exposed in 2 outcrops east of Radford, Va. (localities 11a and 11b, table 1, fig. 1) (Cooper, 1961; Nuelle and Shelton, 1986). South of U.S. Highway 11 at its intersection with Virginia State Route 688 (locality 11a), barite nodules are in the Millboro Shale in the same layers as septarian concretions and also are in overlying layers. The barite occurs in fine-grained, equigranular, oblate spheroidal nodules that, like the concretions, are elongate parallel to bedding. Some have coalesced into aggregates of nodules.

Barite also occurs in veinlets filling fractures in the septarian concretions. The shale in which the concretions occur is dark gray, fissile, and pyritic and has trace fossils on some surfaces. Barite nodules occur in a similar setting in an abandoned quarry on the north side of Route 11, 0.8

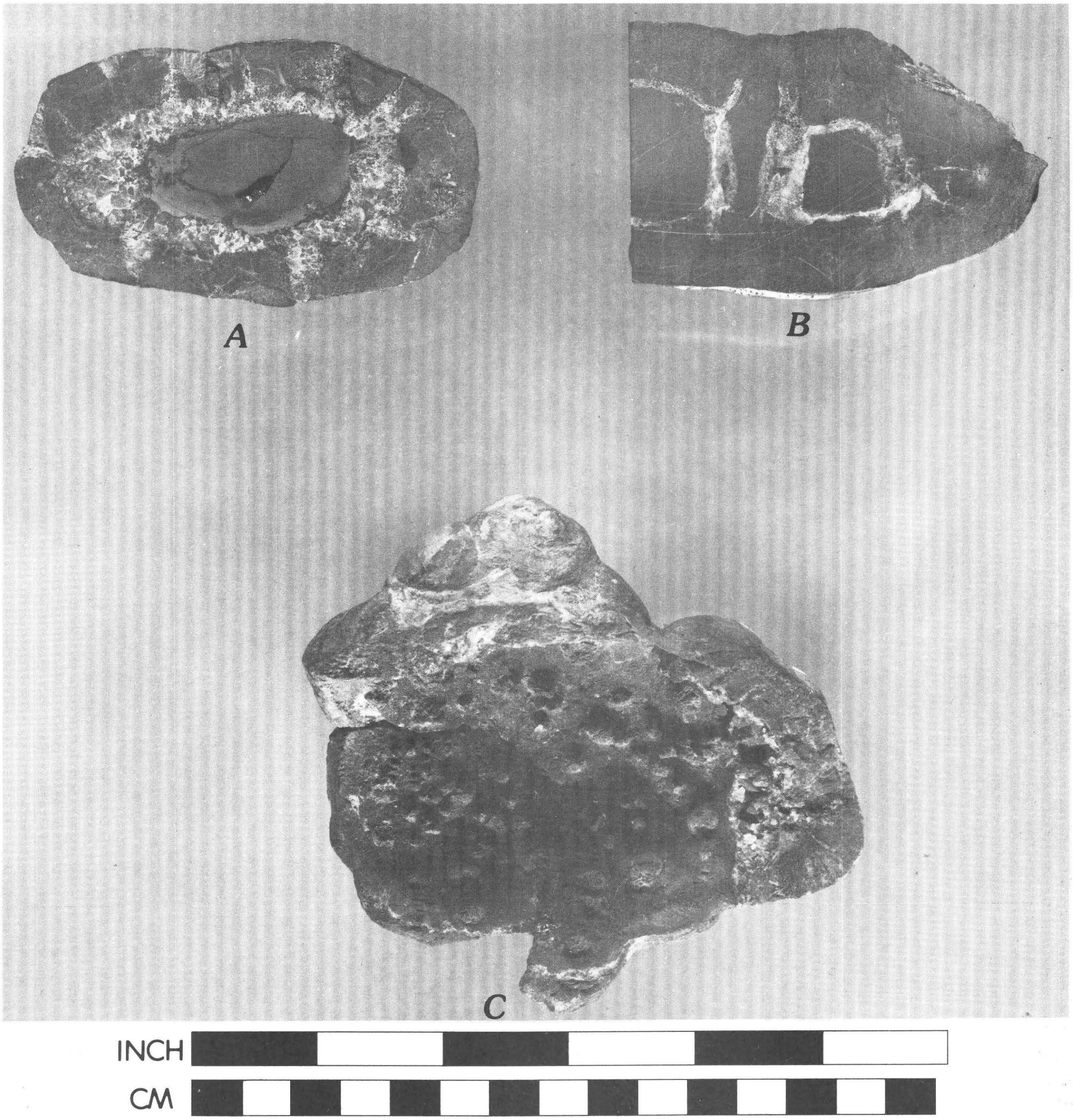

**Figure 6.** Barite nodules from the Williamsville area (locality 7). *A*, Calcareous core, barite rim, and coarse-grained calcite filling the fractures. *B*, Calcareous core and middle layer and barite rim; coarse-grained barite surrounds core and fills the fractures. *C*, Rim of hollow barite nodule.

mi to the east at locality 11b (table 1, fig. 1). The shales in the quarry are intensely sheared, and calcareous concretions, as well as barite nodules, are elongate parallel to the shear planes.

A fragment of coarse-grained, dark-gray barite was found as float on the surface in an area in which there was no outcrop (R.C. McDowell, U.S. Geological Survey, oral commun., 1983), near Little Stony Creek (locality 12, table 1, fig. 1), south of Mountain Lake, Va. The host rock for the barite is not known with certainty but is probably Millboro Shale, on the basis of McDowell's mapping (written commun., 1983). Samples of shales collected from

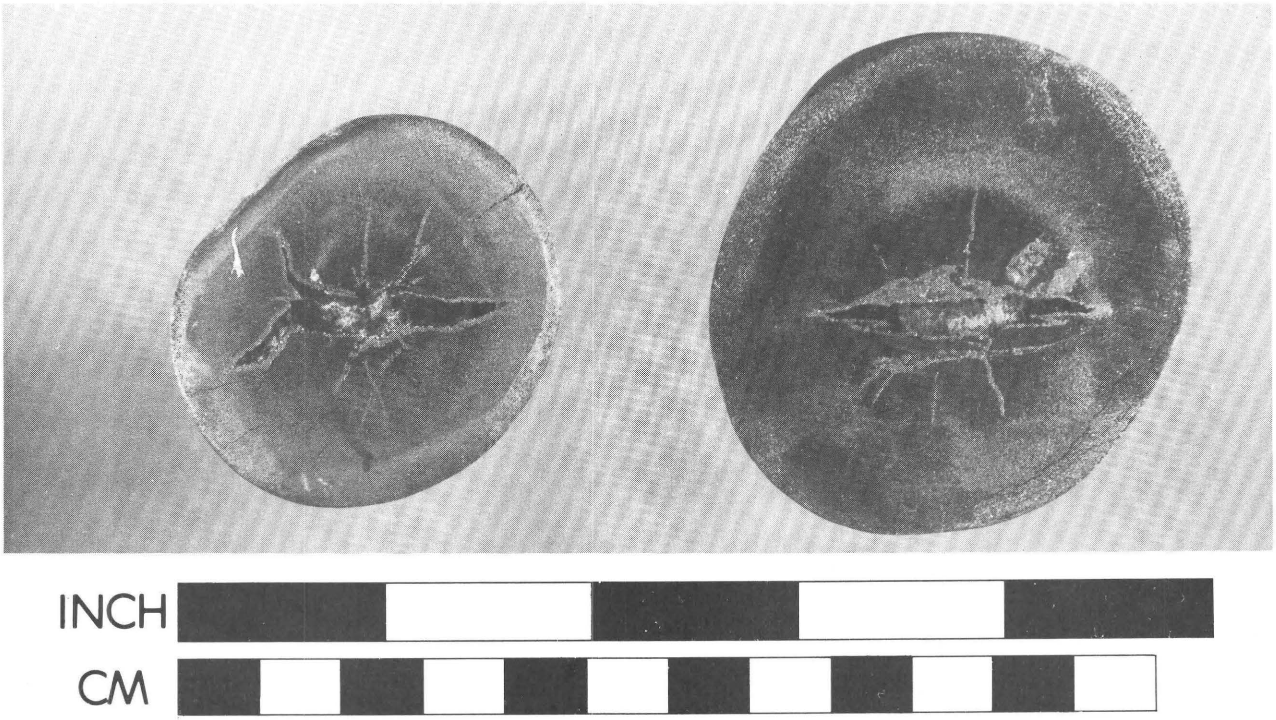

**Figure 7.** Pyritic nodules in which barite fills central fractures in the Millboro Shale near Flood (locality 8).

a few centimeters below the surface are sheared and carbonaceous and have iron oxide coatings.

## GEOLOGIC SETTING AND PALEOENVIRONMENT

In most places the Needmore Shale (Onesquethaw Stage) unconformably overlies the calcareous Oriskany (Ridgeley) Sandstone (Deerpark Stage). The highly fossiliferous Oriskany Sandstone represents the presence in the Appalachian basin of a shallow sea that distributed sand over much of the basin (Dennison and Head, 1975). The Needmore Shale, which grades westward into the Huntersville Chert and the Onondaga Limestone, is mostly light to medium gray, olive gray, or yellowish gray in color and contains a few calcareous layers. Three lithofacies have been distinguished by Dennison (1961)—a black shale lithofacies, a calcitic shale lithofacies, and a calcitic shale and limestone lithofacies. In the Clifton Forge to Williamsville area of western Virginia, where barite nodules are found, the Needmore Shale is less than 25 m thick (Lesure, 1957; Dennison, 1961). It has not been differentiated from the Millboro Shale in mapping of either the Clifton Forge (Lesure, 1957) or Williamsville areas (Bick, 1962).

The lithologic change from the calcareous Lower Devonian Oriskany Sandstone (fig. 2) to the impure calcareous and siliceous Needmore Shale reflects a significant change in depositional environment in the Appalachian basin. Although there was continuous deposition from the Deerpark Stage into the Onesquethaw Stage in the center of the basin, there was a long period of emergence of the rest of the basin at the close of the Oriskany deposition. The relatively deep-water Needmore Shale overlying the Oriskany Sandstone marks the advance of a transgressive sea (Dennison and Head, 1975). The Needmore Shale also marks the first appearance of a Catskill delta facies and is interpreted as representing prodeltaic deposition (Dennison, 1971). The Needmore Shale reflects the beginning of the Acadian orogeny and the development of a basin deep enough to restrict circulation (Ettensohn and Barron, 1981).

Newton (1979) has recognized in the Needmore Shale of Virginia and West Virginia three biofacies corresponding to layers of oxygenation (Rhoads and Morse, 1971) within a stagnant Appalachian basin (fig. 9): (1) an assemblage of diverse, calcareous benthic fauna and bioturbation indicative of aerobic conditions and depths of less than 50 m, (2) an assemblage dominated by bioturbation and trace fossils, probably indicative of a marine worm community from a dysaerobic zone at depths between 50 and 200 m, and (3) laminated black shale that accumulated on an anaerobic ocean floor and contains no benthic or trace fossils. The paleoenvironmental interpretation of water depth for each biofacies is based on analogy with anoxic basins of the Black Sea, Gulf of California, and California Continental Borderland (Rhoads and Morse, 1971; Byers, 1977; Newton, 1979; Ettensohn and Barron, 1981). The black shale lithofacies of Dennison (1961) corresponds to the anaerobic zone, whereas the two lithofacies composed of calcitic shale and limestone correspond to the dysaerobic or aerobic zones (Newton, 1979).

This threefold biofacies-lithofacies suite was recognized at the Hickory Hill barite nodule locality (locality 1). The dark-gray to black shale represents the anaerobic zone and is unfossiliferous except for rare external molds of an inarticulate brachiopod (lingulid), which is probably of planktonic or epiplanktonic habit (J.T. Dutro, Jr., oral commun., 1985). Overlying the dark shale is a zone of lighter colored mudstone that contains sparse pelagic fossils (mostly styliolinids and tentaculitids). The lack of fissility is probably a result of bioturbation. The association of this biofacies and lithofacies is thought to indicate the dysaerobic zone. Overlying the mudstone of the dysaerobic zone is light-colored silty mudstone that contains an abundant benthic epifauna (trilobites, several species of brachiopods, and ostracods) in addition to planktonic or epiplanktonic forms. This assemblage represents an aerobic zone. The mudstone of the dysaerobic and aerobic zones is commonly yellow gray, light olive gray, and light to medium gray or tan. The barite nodules are mostly in the mudstone of the dysaerobic zone and do not occur in rocks of either the anaerobic or the aerobic zones.

All parts of the threefold suite that were identified on Hickory Hill have not been found in other areas, probably because of poor exposures, complexity of structure, and lack of stratigraphic control in the shale units. At locality 7 near Williamsville, the lower, anaerobic portion of the section is composed of fissile, unfossiliferous, dark-gray to grayish-black shale. The rocks of an overlying dysaerobic zone are light-olive-gray mudstones in which the barite nodules occur and which contain only pelagic fossils.

**Figure 8.** Radiating aggregates of bladed barite crystals along a fracture surface at the Mason Cove locality (locality 10).

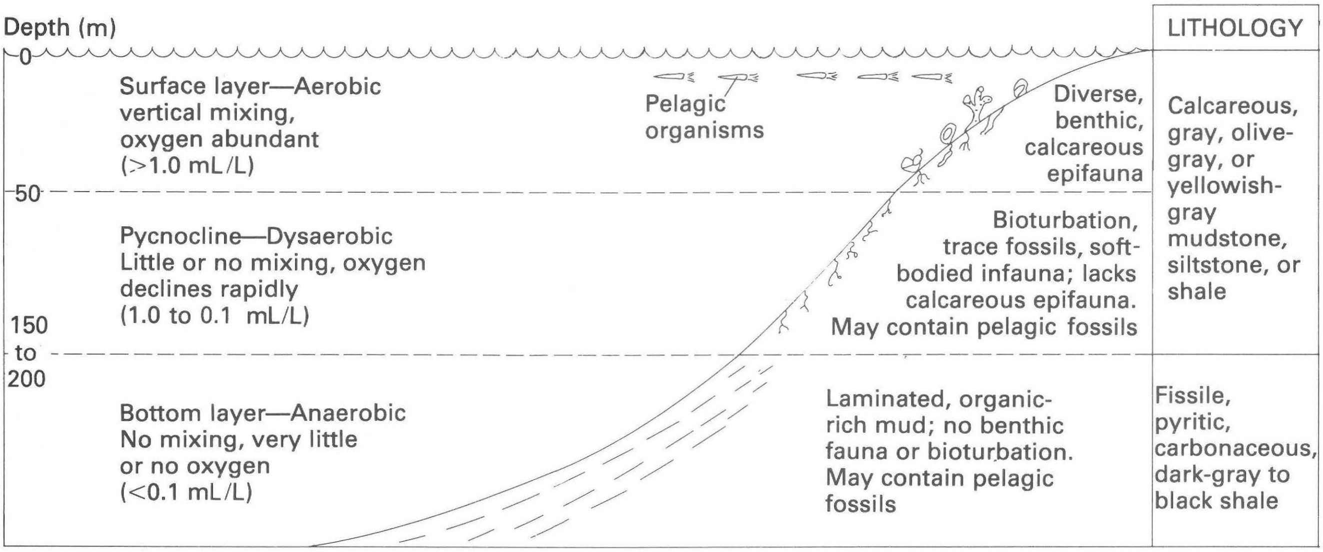

**Figure 9.** Schematic diagram of the Needmore Shale showing relations among degree of bottom oxygenation, biofacies, and depth. Depths are estimates based on the Black Sea, Gulf of California, and the California Continental Borderland. Diagram is adapted from Rhoads and Morse (1971), Byers (1977), Newton (1979), Ettensohn and Barron (1981), and Ettensohn (1985).

Because a bed containing abundant fossils of one species of brachiopod, *Ambocoelia*, is located above the barite nodule zone, the indication is that the conditions were dysaerobic, but approaching aerobic, based on the lack of diversity of species (J.T. Dutro, Jr., oral commun., 1985).

Patterns and associations similar to those described for Hickory Hill and Williamsville are suggested by the occurrence of barite nodules in or near light-colored fossiliferous shales, which are near black fissile shale at Doctors Ridge and near Strom and Williamsville. The barite at these localities is probably in Needmore Shale that was deposited near interfaces between zones of anoxic water and water having higher oxygen levels.

The Tioga Ash Bed (fig. 2), which was derived from a volcanic source and spread throughout the Appalachian basin, marks the top of the Needmore Shale and forms a time marker at the end of the Onesquethaw Stage (Oliver and others, 1968, 1969; Dennison and Textoris, 1977). After the Tioga Ash Bed was deposited, dysaerobic to anaerobic conditions once again developed on the sea floor at the beginning of Erian time, and black organic-rich muds accumulated (Ettensohn and Barron, 1981). The Millboro Shale, deposited from Erian through early Senecan time, is mostly a dark-gray to black shale characterized by the absence of the diverse shelly benthic fauna that is characteristic of oxygenated environments and by the presence of pyritic shale horizons, two characteristics that reflect deposition in dysaerobic to anaerobic marine environments. In addition to the dark-gray to black shales, the Millboro Shale contains several calcareous lenses or concretions, including the Purcell Limestone (member) of Cate (1963) in the lower part and the Tully Limestone (member) in the upper part (Oliver and others, 1968, 1969; Avary, 1979).

Barite nodules are associated with the beds of the Millboro Shale containing calcareous lenses or concretions near Boiling Spring, Pike Pond, Oriskany, Mason Cove, and Radford. Concretions in some of the areas are septarian, and barite is one of the minerals filling the shrinkage fractures in the concretions. Barite nodules generally occur in the same layer as the concretions, in overlying layers, or in both. Where barite nodules are associated with calcareous nodule zones of the limestone members of the Millboro Shale, the associated shale is commonly dark gray to black, laminated, and locally pyritic, factors that suggest that the conditions on the sea floor were dysaerobic or anaerobic. The fact that carbonate concretions could grow indicates that the alkalinity was high enough to allow carbonate precipitation during burial and diagenesis.

The Millboro Shale grades into the overlying Brallier Shale of Senecan age through 30 m or more, changes color from dark to medium gray, and becomes silty; finally, with the introduction of sandstone layers, it becomes the Brallier Shale (Lesure, 1957). The Brallier Shale is a thick sequence of greenish-gray to dark-gray shale interbedded with siltstone and fine-grained sandstone. In some areas, the Brallier Shale contains both brachiopods and pelecypods (Butts, 1940; Lesure, 1957), whose presence indicates a gradual return to an aerobic shallow-water marine environment in the Appalachian basin.

## GEOCHEMISTRY

Geochemical analyses were obtained for representative samples of shale and mudstone from regularly spaced intervals of uniform lithology in and near the barite-bearing beds at the Hickory Hill, Doctors Ridge, Boiling Spring, Strom, Oriskany, Williamsville, Flood, McDowell, Mason Cove, Radford, and Little Stony Creek localities (tables 1 and 2). For comparison, Needmore and Millboro Shales were also sampled in exposures where barite nodules do not occur. These include outcrops along Virginia State Route 615 south of Oriskany to Pine Top (New Castle 7.5-minute quadrangle), along Virginia Route 633 at the north end of Black Oak Ridge east of Green Valley (Green Valley 7.5-minute quadrangle), along Virginia Route 678 southwest of Green Valley (Green Valley 7.5-minute quadrangle), along Virginia State Route 18 east of Jordan Mines (Jordan Mines 7.5-minute quadrangle), and in outcrops outside the barite nodule zones at Hickory Hill and Williamsville (table 3).

Sample intervals ranging from 1 to 8 m across bedding were chosen, and representative composite samples were taken either across consecutive intervals or across uniform lithologies. Samples were analyzed by using two methods: induction coupled plasma–atomic emission spectroscopy (ICP–AES) and semiquantitative optical emission spectrometry (SOES). The ICP–AES analytical technique was used to investigate the applicability of the method to determine the distribution of trace elements in shale. For comparison, the samples also were analyzed by using the conventional SOES method described by Grimes and Marranzino (1968).

Studies of carbonate rocks in southern Missouri demonstrated the usefulness of the ICP–AES method in geochemical investigations of Mississippi Valley-type deposits (Mosier and Motooka, 1983). The method provides rapid, simultaneous, quantitative, multi-element determinations from a single sample preparation technique. Simultaneous measurements of 30 elements can be made in approximately 3 minutes per sample. Of particular interest is the ability to determine trace elements at very low concentration levels without time-consuming concentration procedures.

In preparation for the ICP–AES technique, samples were digested in 6 *N* nitric acid, dried, and dissolved in 20 percent hydrochloric acid. This procedure completely digests carbonate, sulfides, and iron oxides, but most silicate minerals are not broken down. The procedure enhances the detection of ore-related metals and depresses

**Table 2.** Chemical analyses of Needmore and Millboro Shales within and near barite-nodule-bearing beds

[Analyses for elements not in brackets are by semiquantitative optical emission spectrometry. <, less than the lower limit of determination; >, greater than the upper limit of determination; N, not detected. Analyses for elements in brackets are by induction coupled plasma–atomic emission spectroscopy. *, near the limit of determination; —, no data. All analyses are in parts per million. Sample numbers of beds that contain barite nodules are underlined]

| Sample number | Ba | Mn | [Mn] | Ni | [Ni] | Co | [Co] | Zn | [Zn] | Pb | [Pb] | Ag |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Hickory Hill (Needmore Shale)** | | | | | | | | | | | | |
| 181 | 500 | 300 | 326.9 | 70 | 62.84 | 20 | 31.06 | 500 | 224.3 | 10 | 10.29 | N |
| 180 | 500 | 1,500 | 1,911 | 100 | 104.1 | 30 | <6.00 | 200 | 201.3 | <10 | <6.00 | N |
| 179 | 500 | 100 | 58.49 | 70 | 42.17 | 10 | <6.00 | 200 | 198.9 | 20 | 13.70 | <0.5 |
| 176 | 3,000 | 500 | 388.0 | 500 | 509.1 | 20 | <6.00 | <100 | 215.2 | 10 | 6.086 | .5 |
| 175 | 500 | 500 | 530.3 | 100 | 65.42 | 30 | *12.81 | <100 | 91.66 | 10 | 6.9 | N |
| 174 | 700 | 500 | 1,982 | 200 | 343.8 | 70 | 97.69 | <100 | 95.32 | 10 | 7.098 | <.5 |
| 173 | 700 | 2,000 | 5,031 | 70 | 95.33 | 30 | 34.19 | <100 | 52.74 | 20 | 12.36 | N |
| 172 | 1,000 | 1,500 | 1,633 | 100 | 170.9 | 50 | 75.20 | <100 | 67.41 | 10 | <6.00 | N |
| 171 | 1,000 | 1,000 | 1,212 | 70 | 85.86 | 50 | 50.84 | <100 | 62.07 | 15 | <6.00 | N |
| 170 | 1,000 | 700 | 859.5 | 70 | 72.70 | 30 | 31.97 | <100 | 73.22 | 20 | *9.886 | N |
| 169 | 1,500 | 1,000 | 874.9 | 70 | 69.23 | 50 | 39.77 | <100 | 99.73 | 15 | *11.41 | N |
| 168 | 1,000 | 1,000 | 612.5 | 100 | 74.01 | 70 | 29.83 | <100 | 98.94 | 20 | *6.113 | N |
| 167 | 1,000 | 1,000 | 815.8 | 70 | 58.63 | 50 | <6.00 | <100 | 95.23 | 30 | 20.60 | N |
| 166 | 1,000 | 100 | 51.37 | 100 | 48.52 | 20 | 16.97 | <100 | 78.22 | 50 | 23.99 | .5 |
| 165 | 1,000 | 700 | 487.7 | 100 | 57.23 | 30 | <6.00 | 500 | 259.5 | 70 | 38.97 | 2 |
| **Doctors Ridge (Needmore Shale)** | | | | | | | | | | | | |
| 272 | 1,500 | 20 | *1.440 | 10 | *6.609 | N | <6.00 | N | 49.60 | 50 | 25.70 | 2 |
| 373 | 500 | 30 | 3.567 | 15 | *5.660 | N | <6.00 | N | 3.863 | 20 | 15.93 | 1 |
| 274 | 500 | 20 | 3.337 | 20 | *5.783 | N | <6.00 | N | 3.583 | 15 | 19.21 | .7 |
| **Boiling Spring (Millboro Shale)** | | | | | | | | | | | | |
| 821 | 700 | 300 | 430.1 | 50 | 36.51 | 10 | 13.22 | N | 83.47 | 10 | 0.0 | N |
| 822 | 500 | 500 | 630.7 | 30 | 24.51 | 10 | 11.68 | N | 55.37 | 10 | .0 | N |
| 823 | 500 | 700 | 685.5 | 15 | 16.04 | N | 8.02 | N | 46.95 | <10 | .0 | N |
| 824 | 1,000 | 300 | 309.7 | 50 | 33.21 | 10 | 10.25 | N | 41.56 | <10 | .0 | N |
| 825 | 500 | 500 | 516.7 | 30 | 26.51 | 15 | 11.55 | N | 31.60 | 15 | .0 | N |
| 826 | 700 | 700 | 638.6 | 30 | 32.43 | 10 | 11.47 | N | 31.94 | <10 | .0 | N |
| 827 | 500 | 500 | 484.6 | 30 | 21.65 | 7 | 6.86 | N | 41.19 | <10 | .0 | N |
| 828 | 1,000 | 500 | 502.1 | 50 | 27.36 | 10 | 9.12 | N | 36.52 | <10 | .0 | N |
| 829 | 500 | 500 | 549.1 | 20 | 23.85 | 5 | 6.72 | N | 31.87 | <10 | .0 | N |
| 830 | 500 | 700 | 739.5 | 50 | 25.84 | 10 | 8.97 | N | 42.82 | <10 | .0 | N |
| 831 | 500 | 500 | 644.7 | 30 | 28.63 | 10 | 8.17 | N | 41.89 | 10 | 5.17 | N |
| 832 | 500 | 500 | 679.8 | 50 | 47.85 | 20 | 16.94 | N | 44.10 | 20 | 8.48 | N |
| 833 | 500 | 700 | 736.8 | 30 | 27.71 | 15 | 13.09 | N | 31.46 | <10 | .0 | N |
| 834 | 700 | 1,000 | 1,091.3 | 50 | 45.59 | 15 | 18.42 | N | 57.22 | <10 | .0 | N |
| **Strom (Millboro Shale?)** | | | | | | | | | | | | |
| 219 | 700 | 50 | 2.817 | 15 | *3.407 | N | <6.00 | 100 | 7.596 | 50 | 35.76 | 0.7 |
| 218 | 700 | 30 | 2.750 | 15 | *3.541 | N | <6.00 | 100 | 14.16 | 30 | 24.77 | <.5 |
| 217 | 500 | 50 | 2.292 | 10 | <3.00 | N | <6.00 | 100 | 6.438 | 30 | 20.23 | <.5 |
| **Oriskany (Millboro Shale)** | | | | | | | | | | | | |
| 252 | 500 | 500 | 324.5 | 50 | 37.40 | 20 | <6.00 | <100 | 73.51 | 30 | 19.13 | N |
| 253 | 700 | 50 | 8.487 | 20 | 7.626 | N | <6.00 | N | 26.28 | 30 | 26.09 | 0.5 |
| 254 | 1,000 | 30 | 5.989 | 20 | 7.879 | N | <6.00 | N | 31.05 | 20 | 19.22 | .5 |
| 255 | 1,000 | 50 | 14.23 | 30 | 8.870 | N | <6.00 | N | 46.87 | 20 | 18.49 | .5 |
| 256 | 1,500 | 50 | 15.01 | 15 | <3.00 | N | <6.00 | N | 33.22 | 30 | 20.48 | .7 |

**Table 2.** Chemical analyses of Needmore and Millboro Shales within and near barite-nodule-bearing beds—Continued

[Analyses for elements not in brackets are by semiquantitative optical emission spectrometry. <, less than the lower limit of determination; >, greater than the upper limit of determination; N, not detected. Analyses for elements in brackets are by induction coupled plasma–atomic emission spectroscopy. *, near the limit of determination; —, no data. All analyses are in parts per million. Sample numbers of beds that contain barite nodules are underlined]

| Sample number | Ba | Mn | [Mn] | Ni | [Ni] | Co | [Co] | Zn | [Zn] | Pb | [Pb] | Ag |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Williamsville (Needmore Shale)** | | | | | | | | | | | | |
| 283 | 1,500 | 150 | 78.05 | 50 | 46.40 | 20 | <6.00 | N | 115.4 | 15 | *10.26 | N |
| 282 | 1,500 | 300 | 136.9 | 30 | 24.08 | 7 | <6.00 | 200 | 151.9 | N | <6.00 | N |
| 281 | 1,500 | 500 | 732.7 | 70 | 118.7 | 30 | 18.07 | 500 | 650.0 | N | *10.32 | N |
| 280 | 1,000 | 50 | 9.361 | 20 | 15.89 | N | <6.00 | N | 15.24 | 30 | 23.82 | 0.5 |
| 279 | 1,500 | 500 | 289.6 | 50 | 31.64 | 20 | <6.00 | 200 | 216.2 | N | <6.00 | N |
| 278 | 2,000 | 300 | 347.8 | 50 | 56.40 | 15 | <6.00 | <100 | 124.5 | 15 | *8.927 | <.5 |
| 777 | 2,000 | 1,000 | — | 100 | — | 20 | — | <100 | — | 10 | — | N |
| 776 | 2,000 | 500 | — | 50 | — | 15 | — | N | — | 10 | — | N |
| **Flood (Millboro Shale)** | | | | | | | | | | | | |
| 763 | 1,000 | 20 | — | 10 | — | N | — | N | — | 30 | — | 0.5 |
| 764 | 2,000 | 200 | — | 100 | — | 15 | — | N | — | 20 | — | N |
| 765 | 1,000 | 500 | — | 100 | — | 15 | — | <100 | — | 10 | — | N |
| 766 | 1,500 | 100 | — | 50 | — | 5 | — | N | — | 30 | — | 1 |
| 767 | 1,000 | 500 | — | 50 | — | 5 | — | N | — | 10 | — | N |
| 768 | 2,000 | 300 | — | 50 | — | 10 | — | N | — | 10 | — | N |
| 769 | 2,000 | 300 | — | 50 | — | 10 | — | N | — | 10 | — | N |
| 770 | 2,000 | 300 | — | 50 | — | 10 | — | <100 | — | 10 | — | N |
| 771 | 2,000 | 300 | — | 70 | — | 20 | — | 700 | — | 20 | — | N |
| 772 | 3,000 | 5,000 | — | 30 | — | N | — | N | — | 10 | — | N |
| **McDowell (Millboro Shale)** | | | | | | | | | | | | |
| 779 | 2,000 | 500 | — | 150 | — | 20 | — | N | — | 50 | — | 1 |
| 780 | 1,000 | 500 | — | 50 | — | 15 | — | <100 | — | 20 | — | N |
| **Mason Cove (Millboro Shale)** | | | | | | | | | | | | |
| 257 | 500 | 500 | 513.0 | 50 | 29.72 | 15 | <6.00 | N | 35.68 | N | <6.00 | N |
| 258 | 500 | 300 | 278.8 | 70 | 97.71 | 20 | *10.93 | N | 31.67 | 70 | 46.68 | 1.5 |
| 259 | >5,000 | 700 | 635.0 | 70 | 110.6 | 30 | 17.76 | N | 44.14 | 50 | 25.58 | .5 |
| **Radford (Millboro Shale)** | | | | | | | | | | | | |
| 819 | 700 | 500 | 517.1 | 30 | 33.41 | 15 | 14.71 | N | 55.22 | 10 | 0.0 | N |
| 820 | 500 | 70 | 87.7 | 30 | 29.99 | N | 3.86 | <100 | 190.50 | 70 | 89.92 | 0.5 |
| **Little Stony Creek (Millboro Shale?)** | | | | | | | | | | | | |
| 268 | 2,000 | >5,000 | 2,076 | 50 | 78.89 | 30 | *12.72 | 200 | 108.9 | 50 | 24.65 | N |
| 269 | 500 | 70 | 21.89 | 15 | *5.497 | N | <6.00 | N | 5.392 | 50 | 33.59 | 0.5 |
| 270 | 500 | 300 | 407.7 | 20 | 83.49 | 30 | 17.25 | 300 | 227.9 | 20 | *11.45 | N |
| 271 | 300 | 50 | 17.41 | 50 | 14.52 | 5 | <6.00 | N | 20.94 | 30 | 25.04 | .5 |

the influence from metals that reside in lattices of most silicate minerals. A detailed explanation of the procedure is given by Mosier and Motooka (1983). Of the 30 elements identified by SOES and ICP–AES, the elements of most interest in this study are barium, manganese, nickel, cobalt, zinc, lead, and silver, because these elements showed patterns of distribution that seem to be related to the distribution of barite nodule zones. Comparison of the results of SOES and ICP–AES for manganese, nickel, cobalt, zinc, and lead (tables 2 and 3) shows that the results of the two methods are very similar. The SOES results are reported as midpoints (100, 70, 50, 30, 20, 15, 10) of geometric brackets having the boundaries 120, 83, 56, 38, 26, 18, 12, 8.3, and so on. The precision of the SOES method is approximately plus or minus one reporting interval at the 83 percent confidence level and plus or minus

**Table 3.** Chemical analyses of Millboro and Needmore Shales outside of the barite nodule localities

[Analyses for elements not in brackets are by semiquantitative optical emission spectrometry. <, less than the lower limit of determination; >, greater than the upper limit of determination; N, not detected. Analyses for elements in brackets are by induction coupled plasma–atomic emission spectroscopy. *, near the limit of determination; —, no data. All analyses are in parts per million]

| Sample number | Ba | Mn | [Mn] | Ni | [Ni] | Co | [Co] | Zn | [Zn] | Pb | [Pb] | Ag |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **MILLBORO SHALE** | | | | | | | | | | | | |
| **Oriskany area** | | | | | | | | | | | | |
| 208 | 500 | 50 | 8.486 | 15 | *5.324 | N | <6.00 | N | 7.268 | 30 | 21.99 | 1 |
| 209 | 500 | 50 | 10.46 | 15 | *3.999 | N | <6.00 | N | 6.829 | 30 | 21.91 | 1 |
| 223 | 1,000 | 50 | 16.44 | 10 | *3.482 | N | <6.00 | N | 35.55 | 70 | 45.58 | 1.5 |
| 224 | 700 | 70 | 54.61 | 15 | *7.268 | 7 | <6.00 | N | 29.89 | 70 | 37.33 | .7 |
| 225 | 700 | 30 | 6.099 | 7 | <3.00 | N | <6.00 | N | 23.41 | 30 | 21.16 | <.5 |
| 226 | 500 | 50 | 8.172 | 7 | <3.00 | N | <6.00 | N | 28.26 | 30 | 18.79 | N |
| 227 | 700 | 50 | 4.899 | 10 | <3.00 | N | <6.00 | N | 24.07 | 30 | 19.39 | N |
| 228 | 500 | 50 | 6.436 | 10 | <3.00 | N | <6.00 | N | 16.53 | 30 | 18.69 | .5 |
| 229 | 500 | 50 | 5.394 | 15 | *3.190 | N | <6.00 | N | 34.61 | 30 | 16.95 | <.5 |
| 230 | 700 | 50 | 5.504 | 15 | <3.00 | N | <6.00 | N | 16.47 | 30 | 18.52 | N |
| 231 | 500 | 30 | 3.897 | 7 | <3.00 | N | <6.00 | N | 14.07 | 30 | 25.64 | N |
| 232 | 1,500 | 50 | 11.07 | 10 | *4.358 | N | <6.00 | N | 45.67 | 50 | 19.48 | <.5 |
| 233 | 1,500 | 50 | 2.931 | 10 | <3.00 | N | <6.00 | N | 16.20 | 30 | 21.25 | .5 |
| 234 | 1,000 | 50 | 4.206 | 10 | <3.00 | N | <6.00 | N | 26.34 | 30 | 17.90 | 1 |
| 235 | 1,500 | 30 | 2.274 | 10 | <3.00 | N | <6.00 | N | 7.427 | 30 | 16.14 | .7 |
| 236 | 1,000 | 30 | 3.221 | 10 | <3.00 | N | <6.00 | N | 6.419 | 30 | 15.21 | <.5 |
| 237 | 1,500 | 1,000 | 79.50 | 50 | 41.59 | 10 | <6.00 | 200 | 159.5 | 100 | 44.38 | .7 |
| 242 | 1,000 | 30 | 7.89 | 15 | *3.549 | N | <6.00 | N | 27.00 | 30 | 16.76 | <.5 |
| 243 | 1,500 | 30 | 8.552 | 15 | *4.927 | N | <6.00 | N | 12.62 | 30 | 16.88 | <.5 |
| 244 | 2,000 | 30 | 5.366 | 20 | *5.483 | N | <6.00 | N | 13.05 | 50 | 23.95 | N |
| 245 | 1,000 | 50 | 11.04 | 10 | *3.482 | N | <6.00 | N | 22.67 | 20 | 18.36 | <.5 |
| 246 | 1,000 | 30 | 11.38 | 15 | *3.282 | N | <6.00 | N | 20.48 | 30 | 20.56 | N |
| 247 | 1,500 | 70 | 30.91 | 30 | 13.09 | N | <6.00 | N | 42.42 | 30 | 19.66 | N |
| 248 | 700 | 30 | 1.799 | 15 | <3.00 | N | <6.00 | N | 5.389 | 30 | 22.07 | N |
| 249 | 1,500 | 50 | 15.47 | 20 | *4.414 | N | <6.00 | N | 23.09 | 20 | *15.00 | N |
| 250 | 500 | 700 | 428.5 | 50 | 20.40 | 20 | <6.00 | <100 | 58.91 | 20 | <6.00 | N |
| 251 | 1,000 | 500 | 453.1 | 70 | 53.73 | 50 | 17.73 | N | 40.18 | 30 | *13.73 | N |
| **Green Valley area** | | | | | | | | | | | | |
| 137 | 700 | 30 | 7.26 | 20 | <3.00 | N | <6.00 | N | 7.444 | 50 | 24.18 | 1 |
| 138 | 700 | 50 | 9.871 | 20 | *7.481 | N | <6.00 | N | 5.375 | 30 | 18.72 | 1 |
| 139 | 500 | 30 | 4.422 | 20 | *3.156 | N | <6.00 | N | 15.79 | 30 | 20.62 | 1 |
| 140 | 500 | 30 | 4.009 | 20 | <3.00 | N | <6.00 | N | 2.015 | 30 | 20.70 | .7 |
| 141 | 500 | 30 | 2.852 | 20 | *4.542 | N | <6.00 | N | 2.508 | 30 | 20.95 | .7 |
| 142 | 500 | 30 | 2.560 | 20 | <3.00 | N | <6.00 | N | 2.194 | 20 | 18.74 | .7 |
| 143 | 700 | 30 | 3.859 | 50 | *3.383 | N | <6.00 | N | 5.048 | 50 | 22.86 | .7 |
| 144 | 2,000 | 50 | 7.796 | 20 | *5.554 | N | <6.00 | N | 3.620 | 30 | 23.46 | .5 |
| 145 | 1,500 | 50 | 14.67 | 30 | 11.77 | 5 | <6.00 | N | 9.882 | 50 | 29.74 | .7 |
| 146 | 1,500 | 30 | 4.067 | 20 | *6.945 | N | <6.00 | N | 4.813 | 30 | 23.28 | .7 |
| 147 | 1,500 | 50 | 15.81 | 20 | *6.531 | N | <6.00 | N | 11.31 | 30 | 19.53 | .5 |
| 148 | 1,500 | 50 | 7.215 | 50 | 8.331 | N | <6.00 | N | 4.868 | 30 | 21.50 | .7 |
| 149 | 1,500 | 50 | 14.59 | 20 | 16.53 | 7 | <6.00 | 500 | 161.3 | 30 | 23.48 | .5 |
| 150 | 2,000 | 50 | 6.318 | 20 | *6.235 | N | <6.00 | N | 6.408 | 50 | 31.51 | .5 |
| 151 | 2,000 | 50 | 3.228 | 20 | <3.0 | N | <6.00 | N | 1.192 | 30 | <6.00 | .5 |
| 153 | 2,000 | 100 | 58.97 | 20 | 22.44 | 7 | <6.00 | N | 57.45 | 30 | 23.20 | .5 |
| 154 | 2,000 | 200 | 247.8 | 70 | 66.70 | 20 | <6.00 | 200 | 142.3 | 30 | 25.49 | .5 |
| 155 | 2,000 | 200 | 168.3 | 70 | 41.06 | 15 | <6.00 | N | 93.50 | 20 | *13.87 | <.5 |
| 156 | 2,000 | 70 | 30.56 | 30 | 31.12 | 7 | <6.00 | N | 34.86 | 70 | 45.23 | .7 |

**Table 3.** Chemical analyses of Millboro and Needmore Shales outside of the barite nodule localities—Continued

[Analyses for elements not in brackets are by semiquantitative optical emission spectrometry. <, less than the lower limit of determination; >, greater than the upper limit of determination; N, not detected. Analyses for elements in brackets are by induction coupled plasma-atomic emission spectroscopy. *, near the limit of determination; —, no data. All analyses are in parts per million]

| Sample number | Ba | Mn | [Mn] | Ni | [Ni] | Co | [Co] | Zn | [Zn] | Pb | [Pb] | Ag |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Jordan Mines area** | | | | | | | | | | | | |
| 190 | 500 | 70 | 23.76 | 30 | 9.558 | 5 | <6.00 | N | 18.64 | 70 | 40.62 | 0.7 |
| 191 | 500 | 70 | 22.73 | 20 | *6.751 | N | <6.00 | N | 6.77 | 50 | 34.72 | .5 |
| 192 | 700 | 50 | 24.56 | 30 | 28.33 | 5 | <6.00 | N | 14.61 | 50 | 52.57 | .5 |
| 193 | 1,000 | 50 | 18.97 | 50 | 24.02 | 7 | <6.00 | N | 18.58 | 70 | 28.46 | 1 |
| 194 | 3,000 | 70 | 26.15 | 50 | 31.66 | 7 | <6.00 | 200 | 102.2 | 50 | 28.10 | .7 |
| 195 | >5,000 | 30 | 11.84 | 50 | 21.60 | N | <6.00 | N | 32.44 | 50 | 21.28 | 1 |
| 196 | 3,000 | 50 | 8.955 | 50 | 18.53 | 5 | <6.00 | N | 15.14 | 50 | 27.67 | 1 |
| 197 | 2,000 | 50 | 10.51 | 30 | 17.39 | N | <6.00 | N | 7.724 | 50 | 31.25 | 3 |
| 198 | 5,000 | 30 | 10.94 | 30 | 16.05 | N | <6.00 | N | 6.911 | 30 | 23.76 | .7 |
| 199 | 1,000 | 100 | 47.75 | 20 | 10.17 | 5 | <6.00 | N | 35.12 | 30 | 21.47 | <.5 |
| 200 | 700 | 70 | 24.57 | 20 | *7.022 | 5 | <6.00 | N | 16.79 | 50 | 25.08 | .7 |
| 201 | 500 | 100 | 51.34 | 20 | 15.17 | 7 | <6.00 | N | 29.36 | 50 | 32.85 | .7 |
| 202 | 700 | 100 | 64.60 | 20 | 14.29 | 7 | <6.00 | N | 39.65 | 50 | 33.25 | .7 |
| 203 | 700 | 100 | 67.02 | 20 | 18.54 | 5 | <6.00 | N | 35.66 | 50 | 31.14 | .7 |
| 204 | 500 | 300 | 259.7 | 30 | 29.39 | 15 | <6.00 | <100 | 83.03 | 30 | 18.49 | <.5 |
| 205 | 700 | 500 | 362.6 | 70 | 45.36 | 30 | <6.00 | <100 | 28.08 | 50 | 15.04 | .5 |
| 206 | 500 | 100 | 84.92 | 30 | 16.69 | 10 | <6.00 | <100 | 39.56 | 50 | 29.23 | .5 |
| 207 | 1,000 | 70 | 24.55 | 20 | 7.569 | N | <6.00 | <100 | 17.75 | 20 | 24.03 | .7 |
| Hickory Hill area | | | | | | | | | | | | |
| 182 | 700 | 70 | 22.0 | 20 | 7.519 | 5 | *14.16 | N | 4.938 | 100 | 55.89 | 0.7 |
| **NEEDMORE SHALE** | | | | | | | | | | | | |
| **Oriskany area** | | | | | | | | | | | | |
| 239 | 1,000 | 70 | 23.96 | 20 | 7.755 | 5 | <6.00 | N | 71.93 | 100 | 59.60 | 1 |
| 240 | 700 | 70 | 29.54 | 50 | 25.34 | 10 | <6.00 | 200 | 145.8 | 50 | 36.17 | N |
| 241 | 700 | 70 | 30.73 | 30 | 29.96 | 7 | <6.00 | 200 | 147.9 | 50 | 33.54 | N |
| **Green Valley area** | | | | | | | | | | | | |
| 119 | 1,000 | 500 | 346.0 | 70 | 34.62 | 30 | 20.78 | N | 75.60 | N | 9.946 | N |
| 120 | 700 | 700 | 488.9 | 100 | 80.49 | 100 | 98.28 | 200 | 114.6 | 70 | 46.30 | N |
| 121 | 500 | 200 | 129.0 | 50 | 37.82 | 15 | 6.251 | <100 | 30.32 | N | <6.00 | 0.7 |
| 122 | 1,000 | 100 | 26.0 | 50 | 27.29 | 15 | <6.00 | <100 | 32.04 | 20 | *8.733 | N |
| 123 | 1,500 | 50 | 11.33 | 30 | 9.521 | 5 | <6.00 | <100 | 19.27 | <10 | *7.967 | N |
| 124 | 1,000 | 70 | 8.637 | 30 | 9.921 | 7 | <6.00 | <100 | 27.85 | 10 | *7.088 | N |
| 125 | 1,000 | 50 | 3.936 | 30 | <3.00 | 5 | <6.00 | N | 8.212 | 30 | 21.34 | N |
| 126 | 1,000 | 50 | 2.901 | 50 | <3.00 | 10 | <6.00 | N | 14.17 | 30 | *10.31 | N |
| 127 | 1,000 | 50 | 7.054 | 30 | *5.832 | 7 | <6.00 | <100 | 15.56 | 20 | *14.01 | N |
| 128 | 700 | 100 | 50.89 | 30 | *5.884 | 7 | *13.45 | 200 | 57.60 | 100 | 72.88 | .5 |
| 129 | 1,000 | 50 | 3.212 | 50 | <3.00 | N | <6.00 | N | 3.095 | 70 | 38.13 | <.5 |
| 130 | 1,000 | 30 | 3.4 | 15 | <3.00 | N | <6.00 | N | 3.553 | 100 | 53.80 | 1 |
| 131 | 1,000 | 30 | 6.3 | 10 | <3.00 | N | <6.00 | N | 9.562 | 15 | 22.63 | <.5 |
| 132 | 1,000 | 30 | 5.8 | 15 | *3.279 | <5 | <6.00 | <100 | 29.56 | 50 | 18.75 | .5 |
| 133 | 1,000 | 1,000 | 614.2 | 50 | 33.37 | 20 | *11.35 | <100 | 59.77 | 30 | *14.68 | <.5 |
| 134 | 1,500 | 2,000 | 1819 | 70 | 70.76 | 50 | 44.99 | <100 | 124.9 | 30 | 20.02 | N |
| 135 | 1,000 | 500 | 510.1 | 500 | 506.9 | 20 | <6.00 | 700 | 890.5 | 15 | <6.00 | N |
| 136 | 1,000 | 300 | 158.9 | 150 | 117.6 | 10 | <6.00 | 200 | 154.7 | 15 | *6.587 | N |

**Table 3.** Chemical analyses of Millboro and Needmore Shales outside of the barite nodule localities—Continued

[Analyses for elements not in brackets are by semiquantitative optical emission spectrometry. <, less than the lower limit of determination; >, greater than the upper limit of determination; N, not detected. Analyses for elements in brackets are by induction coupled plasma–atomic emission spectroscopy. *, near the limit of determination; —, no data. All analyses are in parts per million]

| Sample number | Ba | Mn | [Mn] | Ni | [Ni] | Co | [Co] | Zn | [Zn] | Pb | [Pb] | Ag |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Jordan Mines area** | | | | | | | | | | | | |
| 183 | 500 | 300 | 234.1 | 50 | 36.92 | 15 | 10.27 | <100 | 45.66 | 30 | 29.94 | N |
| 184 | 500 | 700 | 656.4 | 100 | 100.1 | 30 | 23.98 | <100 | 115.7 | 20 | 18.85 | N |
| 185 | 500 | 300 | 256.3 | 50 | 37.70 | 10 | *7.468 | 200 | 142.4 | 20 | 20.11 | <0.5 |
| 186 | 500 | 50 | 18.43 | 20 | *6.793 | N | <6.00 | N | 9.059 | 70 | 46.61 | 1 |
| 187 | 500 | 70 | 16.36 | 20 | *6.368 | 5 | <6.00 | N | 3.996 | 100 | 59.54 | 1 |
| 188 | 1,000 | 1,000 | 962.6 | 50 | 34.47 | 20 | *7.822 | N | 50.96 | <10 | *6.311 | N |
| 189 | 2,000 | 500 | 356.9 | 70 | 72.02 | 20 | *7.564 | 300 | 231.7 | 50 | 25.92 | 1 |
| **Hickory Hill area** | | | | | | | | | | | | |
| 164 | 3,000 | 50 | 2.265 | 15 | <3.00 | N | <6.00 | <100 | 1.874 | 50 | 23.35 | 1 |
| 163 | 1,500 | 50 | 1.738 | 15 | <3.00 | N | <6.00 | <100 | 1.581 | 30 | 23.61 | 1.5 |
| 162 | 1,500 | 30 | 1.842 | 10 | <3.00 | N | <6.00 | <100 | *1.003 | 100 | 65.31 | 5 |
| 161 | 1,000 | 30 | 1.860 | 15 | <3.00 | N | <6.00 | <100 | *1.040 | 70 | 69.91 | 5 |
| **Williamsville area** | | | | | | | | | | | | |
| 285 | 1,000 | 100 | 31.74 | 30 | 36.07 | 5 | <6.00 | 200 | 161.7 | 30 | 22.89 | 2 |
| 277 | 1,000 | 70 | 34.31 | 50 | 26.42 | 5 | <6.00 | <100 | 123.3 | 20 | 28.21 | 1.5 |
| 275 | 1,000 | 200 | 219.4 | 20 | 35.98 | 15 | <6.00 | N | 26.97 | 30 | 31.69 | N |
| 773 | 1,500 | 20 | — | 15 | — | N | — | N | — | 30 | — | 2 |
| 774 | 1,000 | 20 | — | 15 | — | N | — | N | — | 50 | — | 2 |
| 775 | 3,000 | 20 | — | 20 | — | N | — | N | — | 50 | — | 2 |
| 778 | 1,000 | 20 | — | 5 | — | N | — | N | — | 30 | — | 1 |

two reporting intervals at the 96 percent confidence level (Motooka and Grimes, 1976). Studies on analytical variation for the ICP–AES method have shown the precision to be generally less than ±5 percent except in cases where the detection level is being approached (Mosier and Motooka, 1983, p. 158). Only two significant figures should be considered valid in the ICP–AES results. Where both ICP–AES and SOES results are given in tables 2 and 3, the ICP–AES results are more useful than the SOES results in showing smaller element-concentration variations. In addition, the lower detection limits of the ICP–AES method provide more useful data for elements that are below the detection limits of the SOES method. However, barium results obtained by SOES are more useful than those from ICP–AES, because, with the digestion technique used, barium detected by ICP–AES is from the carbonate form rather than the sulfate form. Silver concentrations determined by the SOES method also are more useful than from ICP–AES, because the former method is more sensitive for this element.

A series of samples across the barite nodule zone in the Needmore Shale on Hickory Hill (locality 1) reveals a distribution pattern for manganese, nickel, cobalt, zinc, lead, and silver (but not barium) that seems to correspond to anaerobic, dysaerobic, and aerobic zones and to the distribution of barite nodules (fig. 10). The lithologic section shows associations of shale and mudstone in each of 20 samples for which analytical results are plotted. The lower, unfossiliferous, anaerobic portion of the section (samples 161 to 164) begins about 3 m above the Needmore-Oriskany contact. Above is a dysaerobic zone of the Needmore Shale (samples 165 to 175) that contains barite nodules in several beds. Overlying the mudstone of the dysaerobic zone is mudstone of an aerobic zone of the Needmore Shale containing an abundant benthic epifauna (samples 176 to 181). Above is unfossiliferous, dark-gray Millboro Shale (sample 182).

The pattern of distribution of barium in the shale and mudstone bears no obvious relation to the barite nodule zone. However, because the barite nodules locally compose 2 to 4 percent of some shale layers, the overall barium content of the barite-bearing layers would be on the order of 10 times higher than that of other shales if barite nodules were to be proportionately included in the samples. Mudstone from the aerobic and dysaerobic zones has higher values of manganese, nickel, cobalt, and zinc than shale from the underlying and overlying anaerobic zones. Distribution of lead and silver follows the opposite pattern, with low concentrations in shale and mudstone from the aerobic and dysaerobic zones and higher concentrations in shale from anaerobic zones.

The pattern of distribution of barium, manganese, nickel, cobalt, zinc, lead, and silver relative to lithofacies, biofacies, and barite nodule zones at Williamsville (fig. 11) is similar to that observed for Hickory Hill but is less pronounced. The mudstone from the dysaerobic zone is slightly enriched in manganese, nickel, cobalt, and zinc relative to the shales from the anaerobic zone. Shale from the anaerobic zone is slightly enriched in lead and silver relative to mudstone from the dysaerobic zone. The content of barium in the shales, as at Hickory Hill, seems unrelated to the barite nodule zones. The elemental concentrations measured are roughly equivalent to average values for clays and shales.

Histograms (fig. 12) show the distribution of these elements in samples of shale from localities that did not contain barite nodules for comparison with shale samples from localities where barite occurs. The histograms depicting the chemical data confirm that there is no significant elevation in the barium content of host rocks from barite nodule zones ("barite matrix" on fig. 12) over that in shale or mudstone that does not contain barite nodules ("no barite" on fig. 12). In samples from the Millboro Shale, the mean value for barium was actually less for shale from the barite nodule zones than for other samples from the Millboro Shale.

Manganese, nickel, cobalt, and zinc concentrations are slightly higher in the Needmore Shale than in the Millboro Shale (fig. 12). Manganese has a bimodal pattern of distribution in both the Needmore and Millboro Shales. Values of 500 parts per million (ppm) and greater were found primarily in samples from barite nodule localities. That pattern suggests enrichment in manganese in the sediments where barite nodules formed. Nickel has a roughly normal distribution in shale and mudstone that are not from barite nodule localities. Comparison of distribution patterns and means for nickel suggests a slight enrichment in the barite nodule localities. Cobalt and zinc were not detected in many samples, and means could not be calculated. Comparison of histogram patterns, showing higher amounts of both metals in shale and mudstone associated with barite nodule zones, especially from the Needmore Shale, indicates slight enrichment in cobalt and zinc in those zones.

The histogram for lead shows a high frequency of values of 30 ppm in the Millboro Shale that does not contain barite nodules and a greater variation in the Needmore Shale and Millboro Shale that are matrix shales for barite nodules. The means and distribution patterns for lead in both the Needmore and Millboro Shales show a slight depletion of that metal in the barite nodule zones compared with shale and mudstone that do not have barite nodule zones.

The histograms for silver show slightly lower values in the Needmore Shale than in the Millboro Shale. The distribution pattern shows a slight decrease in frequency of higher values in shales and mudstones from barite nodule zones, especially in the Millboro Shale.

In summary, the geochemical data show (1) no significant elevation in barium content of the host rocks in which the barite nodules occur over shale and mudstone that do not contain barite nodules, (2) higher manganese, nickel, cobalt, and zinc and lower lead and silver contents in the Needmore than in the Millboro Shale, and (3) higher manganese, nickel, cobalt, and zinc and lower lead and silver contents in host rocks of barite nodules than in shale and mudstone that do not contain barite.

## SULFUR AND OXYGEN ISOTOPE AND FLUID INCLUSION STUDIES

Sulfur and oxygen isotope values have been determined for Devonian bedded and nodular barite from western Canada (Cecile and others, 1983), central Nevada (Rye and others, 1978), and the Appalachian basin (Nuelle and Shelton, 1986). In each of these studies (table 4), barite nodules had a large range of $\delta^{34}S$ and $\delta^{18}O$ values. Average values for both $\delta^{34}S$ and $\delta^{18}O$ are considerably heavier than Devonian seawater sulfate values, which are approximately $\delta^{34}S$ = 17 to 27 per mil and $\delta^{18}O$ = 15 to 17 per mil (Claypool and others, 1980; Cecile and others, 1983). In contrast, sulfur isotope values for barite from thick beds in stratiform deposits of western Canada, Arkansas, and Nevada and for stratiform lead-zinc-barite deposits at Meggen and Rammelsburg (Germany) are close to the coeval seawater sulfate values (table 5).

**Table 4.** Sulfur and oxygen isotope values of barite nodules (including rosettes and concretions) of Devonian age
[—, no data]

| $\delta^{34}S$ (per mil) | | $\delta^{18}O$ (per mil) | | | | |
|---|---|---|---|---|---|---|
| Range | Average (number of samples) | Range | Average (number of samples) | Age | Location | Reference |
| 41.8–53.0 | 46.3 (4) | 20.3–29.1 | 23.3 (4) | Late Devonian | Western Canada | Cecile and others, 1983. |
| 29.1–56.3 | 38.7 (13) | — | — | Late Devonian | Central Nevada | Rye and others, 1978. |
| 28.0–47.4 | 38.5 (9) | 19.3–30.4 | 24.6 (4) | Middle Devonian | Western Maryland | Nuelle and Shelton, 1986. |

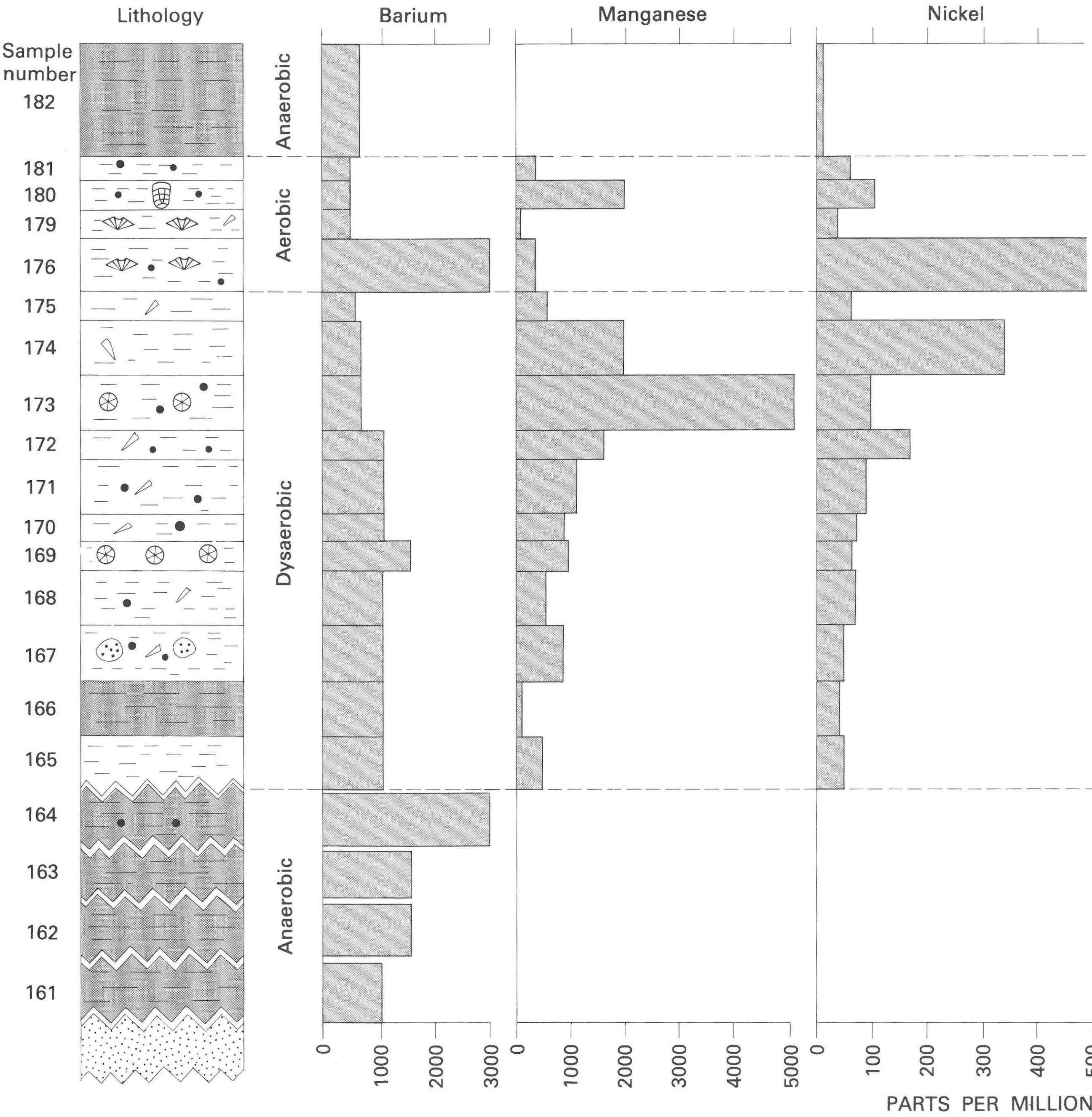

**Figure 10.** Stratigraphic variation in the distribution of barium, manganese, nickel, cobalt, zinc, lead, and silver at Hickory Hill (locality 1). The lithologic section shows association of shales and mudstones for each of the 20 samples for which analytical results are plotted. Samples are representative of 1- to 4-m intervals. Graphs are from induction coupled plasma–atomic emissions spectroscopy (ICP–AES) analyses for all elements except barium and silver, for which results of semiquantitative optical emission spectrometry (SOES) analyses are plotted. Results for ICP–AES analyses that are less than the lower limit of determination are plotted as zero. Results of SOES analyses in which the element was detected but is less than the lower limit of determination are plotted at one-half the limit of determination for that element; if an element was not detected, the results are plotted as zero. Data are given in tables 2 and 3. Numbers in parentheses refer to the rock-color chart of Goddard and others (1948).

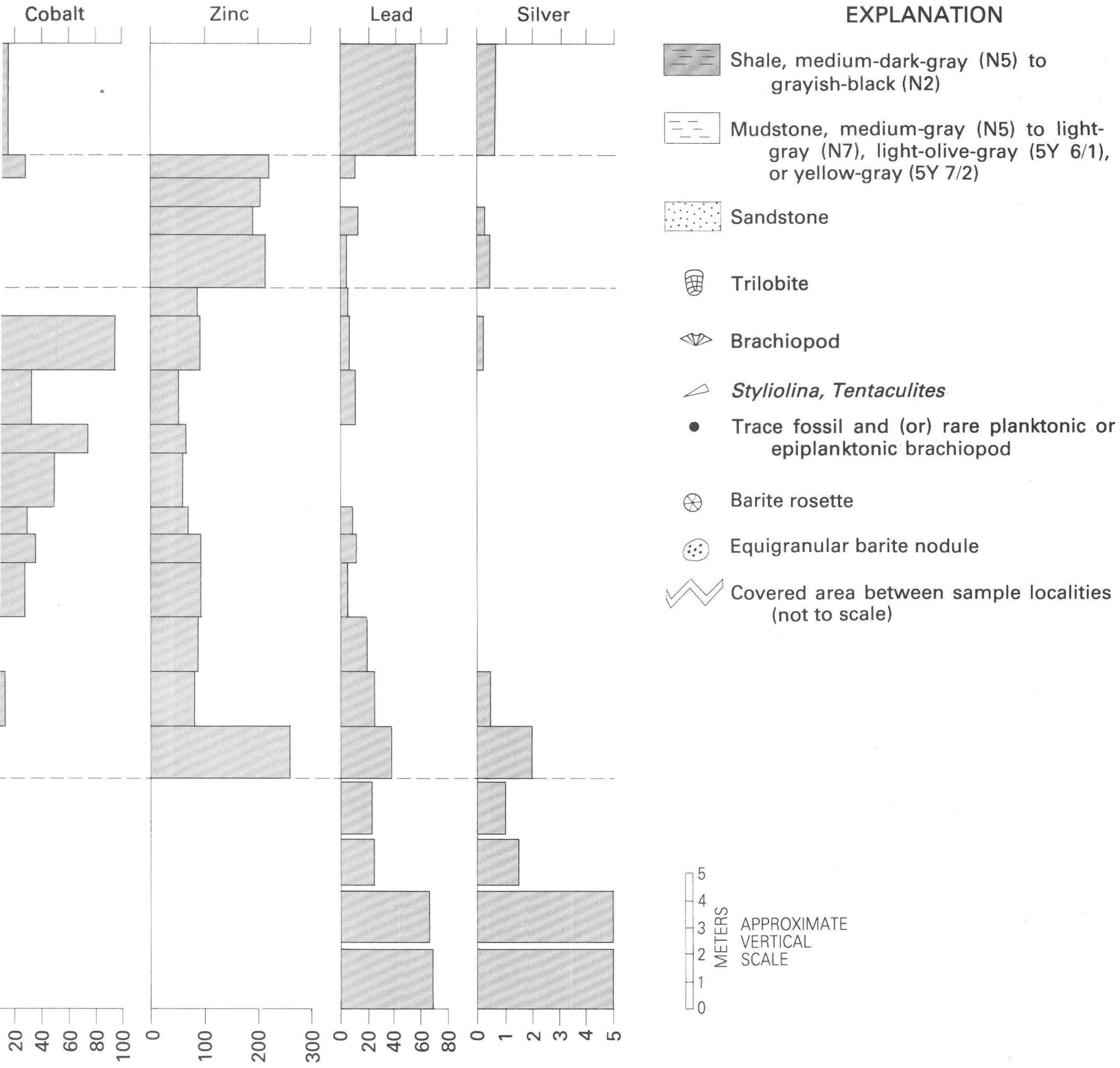

**Figure 10.**—Continued.

Nuelle and Shelton's data (1986) showed a systematic increase in $\delta^{34}S$ (28.0 to 44.1 per mil) with size and proximity to a zone of larger and more abundant nodules in samples collected along a single traverse at a locality where barite nodules occur in and immediately above the Purcell Limestone Member of the Middle Devonian Marcellus Shale (table 6). They noted a slight decrease in $\delta^{34}S$ in the transition from large, abundant nodules (42.5 and 44.1 per mil) to coalescing nodules (40.8 per mil).

Oxygen isotope values for the barite nodules (tables 4 and 6) (Nuelle and Shelton, 1986) are considerably elevated in $^{18}O$ relative to Devonian seawater sulfate values ($\delta^{18}O$ = 15 to 18 per mil; Claypool and others, 1980). Sulfate oxygen isotopic ratios are heavier in barite from horizons containing coalesced nodules as compared to intervals containing smaller, less abundant, isolated nodules (25.7 per mil vs. 23.0 per mil, respectively).

Fluid inclusions from barite nodules (tables 4 and 6) from the Appalachian basin have not been studied because the nodules are too fine grained to contain suitable inclusions. Data for primary and pseudosecondary fluid inclusions were reported by Nuelle and Shelton (1986) for vein

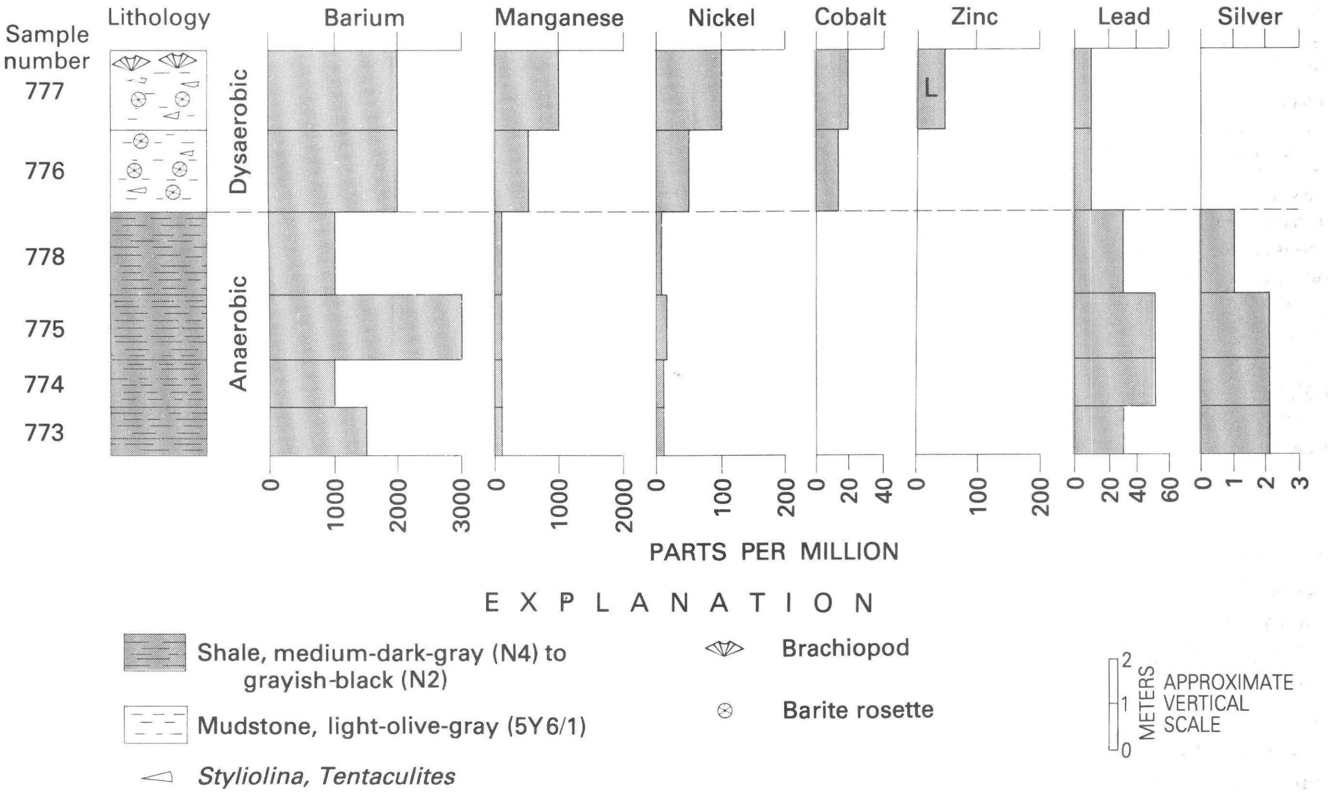

**Figure 11.** Stratigraphic variation in the distribution of barium, manganese, nickel, cobalt, zinc, lead, and silver near Williamsville (locality 7). The lithologic section shows associations of shales and mudstones for each of six samples for which analytical results are plotted. Samples are representative of 1- to 1.5-m intervals. Graphs are from semiquantitative optical emission spectrometry analyses. L, the element was detected but below the limit of determination; the analysis is plotted at one-half the limit of determination for that element. If an element was not detected, the results are plotted as zero. Data are given in tables 2 and 3. Numbers in parentheses refer to the rock-color chart of Goddard and others (1948).

**Table 5.** Sulfur and oxygen isotope values of stratiform barite of Devonian age

[— , no data]

| $\delta^{34}S$ (per mil) | | $\delta^{18}O$ (per mil) | | Age | Location | Reference |
|---|---|---|---|---|---|---|
| Range | Average (number of samples) | Range | Average (number of samples) | | | |
| 23.2–29.7 | 27.0 (3) | 16.2–19.5 | 17.9 (3) | Middle to Late Devonian. | Western Canada | Cecile and others, 1983. |
| 20.9–28.6 | 24.4 (10) | — | — | Late Devonian | Central Nevada | Rye and others, 1978. |
| 14.6–26.8 | 28.8 (72) | — | — | Middle Devonian | Meggen, Germany | Buschendorf and others, 1963. |
| 13.2–28.8 | 22.4 (68) | — | — | Middle Devonian | Rammelsburg, Germany (main ore lenses). | Anger and others, 1966. |
| 27.4–34.1 | 30 (22) | — | — | Middle Devonian | Rammelsburg, Germany (sulfide-free barite lens). | Anger and others, 1966. |

**Table 6.** Sulfur and oxygen isotope data for barite nodules from a locality near Spring Gap, Md. (From Nuelle and Shelton, 1986)

[—, no data]

| Sample description | $\delta^{34}S$ (per mil) | $\delta^{18}O$ |
|---|---|---|
| 8-cm nodule, 20 m from zone of abundant nodules. | 28.0 | 23.0 |
| 8-cm nodule, 16 m from zone of abundant nodules. | 32.6 | — |
| 10-cm nodule, 15 m from zone of abundant nodules. | 33.1 | — |
| 15-cm nodule, from zone of abundant nodules. | 42.5 | — |
| 16-cm nodule, from zone of abundant nodules. | 44.1 | — |
| Bed of coalescing nodules .............. | 40.8 | 25.6 |

and vug-filling barite and for large (up to 10 mm wide) barite crystals from nodules. The barite yielded homogenization temperatures of 72 °C to 142 °C and salinites ranging from 23.1 to 15.6 equivalent weight percent NaCl. However, all of the data are from barite that crystallized later than the barite nodules (Nuelle and Shelton, 1986) and do not provide information on temperatures and salinities of the mineralizing fluid. Because the inclusions are from barite in intensely deformed rocks, the high temperatures may be indicative of deep burial conditions or orogenic effects. In addition, these temperatures may be artifacts of stretching or leaking of the inclusions.

# DISCUSSION

## Paleoenvironment

The physical characteristics and lithologic associations of the barite nodules provide information about the type of depositional environment in which the nodules formed. The deformation of laminae in the enclosing shales around nodules (fig. 5) indicates that growth of the nodules began in unconsolidated sediment (Raiswell, 1971). Such features as the larger crystals that formed at the center or around a hollow core of the radiating barite (fig. 3) and the association of barite in alternating layers with calcite and pyrite (figs. 6 and 7) suggest deposition under fluctuating chemical conditions. The presence of septarian structures in some calcitic and pyritic nodules indicates that the nodules formed in highly porous, water-rich sediment and that fissures developed in the nodules during water loss and contraction. These features suggest that the nodules formed during early diagenesis in response to fluctuations in chemical conditions that existed when the surrounding sediments were still unlithified.

Dysaerobic and anaerobic conditions prevailed throughout much of the Appalachian basin during deposition of the Needmore and Millboro Shales. However, the local presence of a varied benthic calcareous epifauna is evidence that aerobic conditions existed locally. Barite nodules are associated with zones of light-colored shales that lack benthic epifauna but contain evidence of bioturbation and pelagic forms. This association suggests that barite nodules formed in sediments deposited in dysaerobic zones. The occurrence of barite nodule zones below aerobic zones and above unfossiliferous black shale is indicative of fluctuating conditions. Where barite nodules are associated with zones of calcareous and pyritic nodules in limestone members (Purcell and Tully Limestones) of the Millboro Shale, the shales are commonly dark gray to black, laminated, and locally pyritic. This relation suggests that the conditions in the muds were dysaerobic to anaerobic. Therefore, the paleoenvironmental indications from the sedimentary rocks in which the barite nodules occur are that nodules formed in oxygen-deficient marine environments (1) in stratigraphic positions recording dysaerobic bottom conditions and (2) in association with layers containing calcareous and pyritic nodules that formed in anaerobic to dysaerobic zones. The barite nodules have not been found in the shales representing aerobic environments or in shales from anaerobic environments, except in association with carbonate.

## Redox Fronts

Although the barite nodules in the shales and mudstones have a wide distribution both geographically and stratigraphically (Clark, 1985, 1986a,b, 1987), the occurrences are restricted to specific paleoenvironmental conditions, and distribution may be controlled, at least in part, by oxidation conditions. If barium were present in the anoxic portion of the water column, barite would be expected to precipitate in the oxygenated portion of the reduction-oxidation (redox) front (fig. 13). This electrochemical transition may have been present in the water column or within pore waters. Precipitation of barite at redox borders has been suggested by Cecile and others (1983), Clark, (1985, 1986a,b), and Nuelle and Shelton (1986). Geologic relations in western Virginia show that redox boundaries are indeed the locus of barite nodule formation.

In addition to inorganic mechanisms, microbes may play a significant role in concentrating elements at redox boundaries by serving as a catalyst. Sorokin (1964, 1966) has documented large populations of both aerobic and anaerobic bacteria (*Thiobacilli*) and high rates of chemosynthesis in the boundary layer between the aerobic zone and the anaerobic zone in the water column of the Black Sea. The coincidence of a high rate of bacterial biosynthesis with the changes in concentrations of certain elements at the boundary layers suggests that the bacteria may play a role

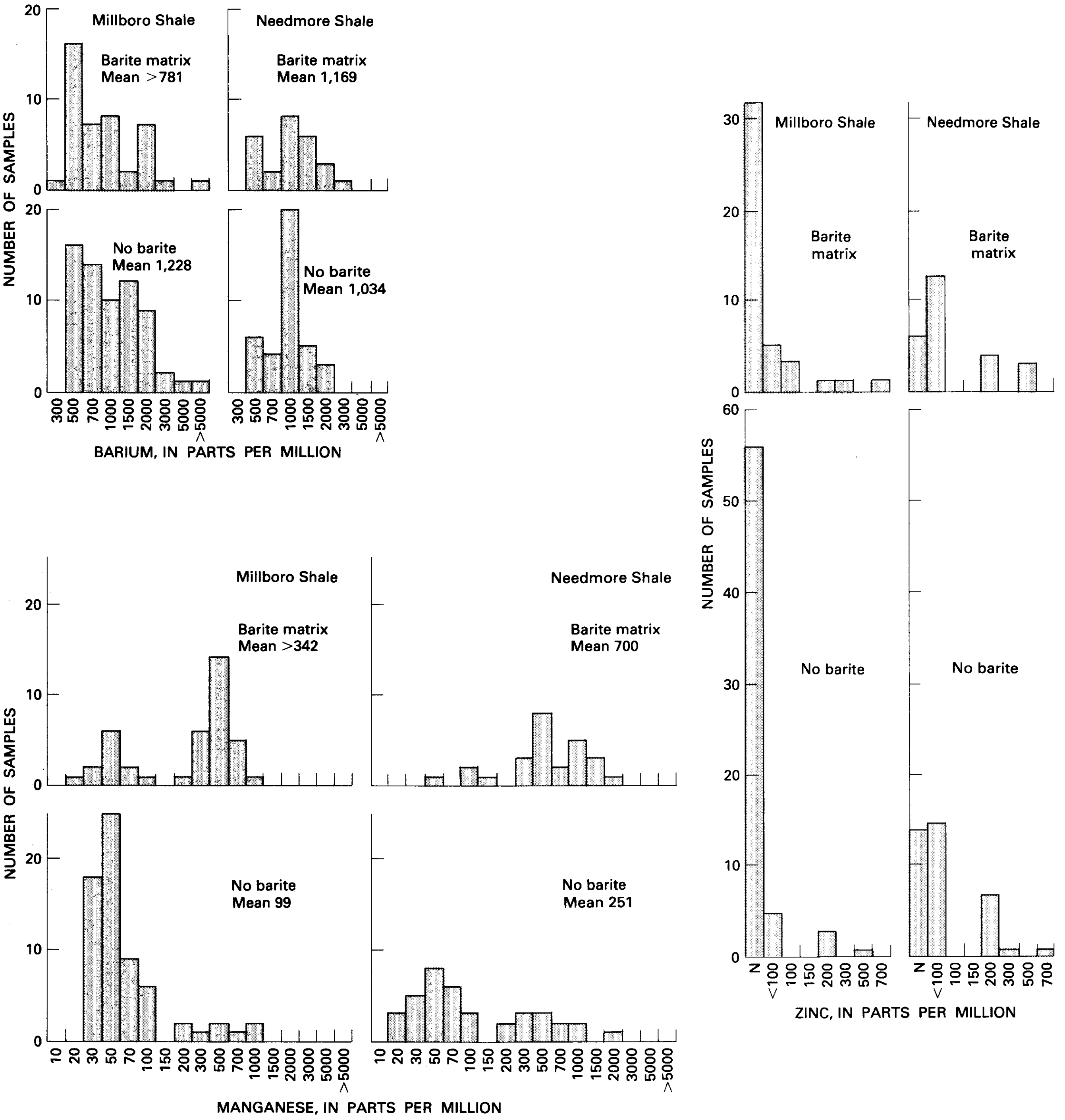

**Figure 12.** Histograms of 173 semiquantitative spectrographic analyses of barium, manganese, nickel, cobalt, zinc, lead, and silver in the Millboro Shale and Needmore Shale. N, not detected; <, less than lower limit of determination; >, greater than upper limit of determination. For data sets having five or fewer analyses that were greater or less than the detection limits, mean values were calculated by using the detection limit and are identified by the symbol > or <. When more than five analyses were less than or greater than the detection limits, means were not calculated. Data are given in tables 2 and 3.

in the reactions taking place at redox boundaries in pore waters.

The observed association of barite and carbonate nodules in anaerobic zones can be explained in several ways. The precipitation of barite from anoxic pore water may be a result of slight increases in pH (fig. 13). Weeks (1953) observed that carbonate-concretion-bearing shales were deposited generally in stagnant-water environments that are unfavorable for the formation of carbonate because of their low alkalinity. Weeks (1953) suggested that an

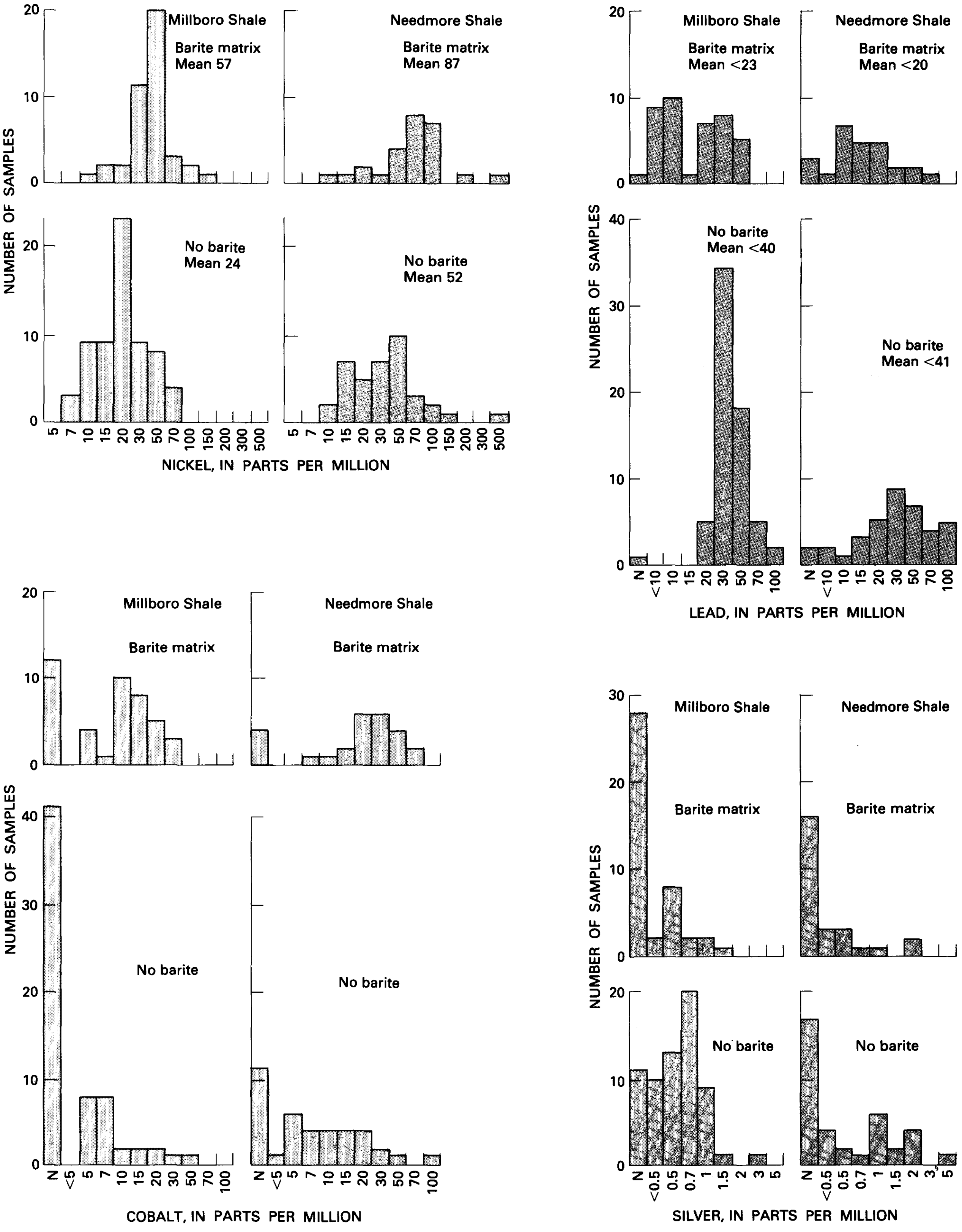

**Figure 12.**—Continued.

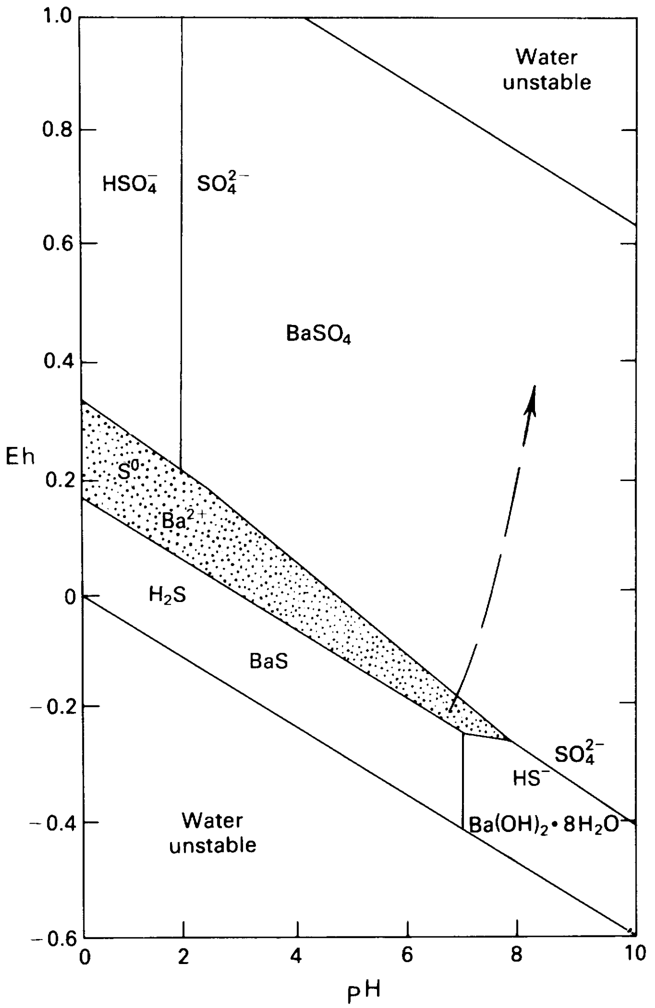

**Figure 13.** Eh-pH diagram for the system Ba-S-$H_2O$ at 25 °C, with 1 atmosphere total pressure and total dissolved sulfur species = $10^{-1}$. Adapted from Schmitt (1962). The dotted area is the field of soluble $Ba^{2+}$. The long arrow shows the change in Eh-pH conditions of the Black Sea; these changes range from deep, anoxic bottom water to oxidized surface water (from Cannon and Force, 1983).

alkalinity adequate for carbonate deposition may be created locally by the ammonia that evolves during the decomposition of organic matter. Berner (1968) showed that an increase in pH and the precipitation of calcium from solution were produced by the action of anaerobic bacteria in the decomposition of organic matter. Bacterial decay of tests of microorganisms has been postulated by Blome and Albert (1985) to provide the alkaline environment and $CO_2$ necessary for development of carbonate concretions. The tests of the microorganisms may have escaped dissolution during descent through the water column because they were encased in fecal pellets, which disintegrated because of bacterial action when they reached the sea floor (Blome and Albert, 1985). The association of barite with carbonate concretion zones in black shales suggests that similar processes may account for the precipitation of both barite and calcite in anoxic environments. The precipitation of barite can be explained by local increases in alkalinity associated with decay of organic matter in the presence of barium ions in solution in anoxic water. Because of its solubility in a reducing environment, barite may dissolve again. However, the presence of carbonate minerals, which help to buffer pH, may permit sulfate to remain stable under slightly reducing conditions (Church, 1970; Bjorlykke and Griffin, 1973).

## Sulfur and Oxygen Isotopes

Enrichment in $^{34}S$ and $^{18}O$ isotopes in barite can be caused by preferential removal of $^{32}S$ and $^{16}O$ from the soluble sulfate pool by sulfate-reducing bacteria. The presence of high concentrations of the heavy isotopes in the barite nodules of the Appalachian basin compared to heavy isotopes in Devonian seawater strongly suggests that the sulfate ions were subjected to extensive action of sulfate-reducing bacteria. The enrichment indicates also that rates of barite precipitation were slow compared to rates of sulfate dissolution and reduction (Cecile and others, 1983). Alternatively, the amount of enrichment may reflect the degree to which the system is closed in regard to exchange with normal seawater, the isotopic composition of the sulfate pool, the rate of sulfate reduction, the rate of sedimentation, and the rate of removal of isotopically light sulfur.

Nuelle and Shelton (1986) suggested that the barite nodules in the Appalachian basin may represent fringe areas of larger massive barite deposits and that such deposits would have sulfur and oxygen isotope compositions near that of coeval seawater, as is the case for many stratiform barite deposits. An increase in $^{34}S$ content of sulfate in barite nodules relative to increasing size and proximity to a zone of large, abundant nodules (table 6; fig. 14) was noted. Nuelle and Shelton (1986) explained the heavy isotope enrichment in the barite nodules as the result of decreased biogenic influence away from the barite source. Enhanced activity of sulfur-reducing bacteria near a submarine-spring barium source is inferred (Nuelle and Shelton, 1986).

Alternative explanations of Nuelle and Shelton's (1986) data are feasible. The heavy isotope enrichment may be the result of enhanced activity of sulfur-reducing bacteria at a redox interface. The existence of a concentration gradient between barium in solution in anoxic hydrogen sulfide waters and more oxygenated sulfate waters can account for migration of barium toward the redox interface and the increase in barite concentrations. The heavy isotope enrichment may reflect repeated cycles of sulfate dissolution and precipitation (Cecile and others, 1983), concentrations of heavier sulfates in pore waters of anoxic zones, or a combination of these and other factors.

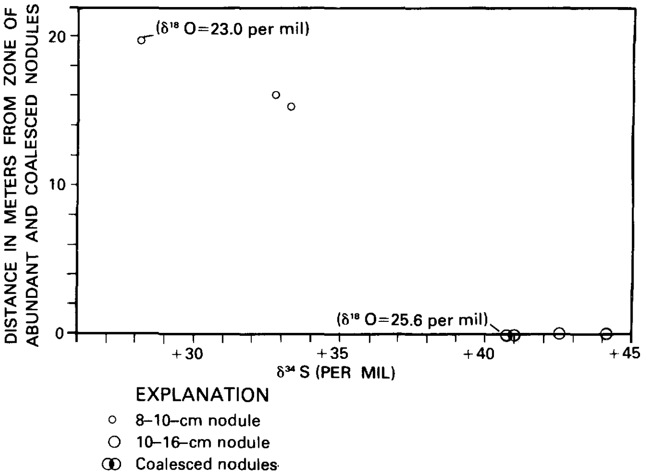

**Figure 14.** Increase in $\delta^{34}S$ relative to increasing size of nodules and proximity to zone that contains large, abundant nodules and coalesced nodules. (Data from Nuelle and Shelton, 1986; table 6).

## Geochemical Patterns

The pattern of enrichment of manganese associated with barite nodule zones and the more oxidized sedimentary rocks of the Needmore Shale relative to the rocks of the anoxic zones suggests a relation between the distribution of barite and manganese. On the basis of Eh-pH relations, both barite and manganese would be expected to be soluble in anoxic waters, and barite precipitation would be expected at more negative Eh conditions than would manganese oxide precipitation (Cannon and Force, 1983; fig. 13).

Profiles of dissolved manganese, iron, copper, and nickel across boundaries between oxygenated surface waters and sulfide-containing deep waters demonstrate the effect of redox reactions on the distribution patterns (Spencer and Brewer, 1971; Jacobs and Emerson, 1982). The concentrations of manganese and iron in the sulfide-containing deep water greatly exceed those of oxygenated surface water, while copper and zinc concentrations are depleted in the deep water. The association of barite nodules with shales of higher manganese content in the dysaerobic portions of the sedimentary sequence rather than in the anaerobic portions supports a concept of solution and reprecipitation of both barium and manganese compounds in response to local changes in Eh and pH.

The patterns of distribution of nickel, cobalt, and zinc at the Hickory Hill and Williamsville localities and in samples from the Needmore Shale compared to the Millboro Shale are similar to the patterns of manganese distribution in those rocks. Enrichment of these elements is in shales and mudstones from aerobic and dysaerobic environments relative to shales and mudstones from anaerobic environments. If nickel, cobalt, and zinc were present in sulfide minerals, precipitation would be expected under anaerobic conditions. Inorganic mechanisms that can explain the association of barite with increased amounts of manganese, nickel, cobalt, and zinc in shales and mudstones above the anaeorobic-dysaerobic interface are metallic complexing, adsorption, and coprecipitation.

The formation of thiometallic and perhaps organometallic complexes is suspected in interstitial waters of marine sediments because of the lack of agreement between calculated and naturally occurring concentrations (Spencer and Brewer, 1971). Adsorption of metals on negatively charged surfaces is another possible explanation for the similarity of distribution patterns of manganese, nickel, cobalt, and zinc. Transition-metal ions adsorb strongly on hydrous manganese dioxide in this order of selectivity: Co >Mn >Zn >Ni >Ba >Sr >Ca >Mg (Murray, 1975). The possibility of coprecipitation is suggested by the observed enrichment in zinc, nickel, cobalt, and copper in marine oxides, which can be attributed, at least in part, to atomic substitution in the lattice of todorokite (a hydrated manganese oxide) (Burns and Burns, 1979).

## Barium Source

An important factor regarding the origin of barite nodules is the source of the barium. Normal seawater can provide an adequate source of sulfate ions to precipitate barite (Dean and Schreiber, 1978). However, the source of the barium is problematic because the amount of barium present in normal seawater is very small. The ultimate source of the barium in seawater is significant in evaluating the potential for the occurrence of economically important barite deposits. Some of the ultimate means by which barium enters seawater, as suggested in the literature, are by the (1) introduction of hydrothermal fluids by submarine springs, (2) remobilization from bedded barite deposits, (3) introduction with or in volcanic rocks, and (4) redistribution from the sedimentary pile.

Derivation of barium from some form of hydrothermal fluid, such as formation waters brought to the surface of the ocean floor as submarine springs, is the probable source of barium for many large, economically significant deposits. Introduction of barium in hydrothermal fluids has been suggested for many large, bedded barite deposits, such as in Nevada and Arkansas (Hanor and Baria, 1977; Hanor, 1982; Brobst, 1984; Papke, 1984; Poole, 1986), for stratiform barite base-metal deposits (Large, 1981), and for some barite nodules on the ocean floor (Revelle and Emery, 1951).

The enrichment of manganese, nickel, cobalt, zinc, lead, and silver described above resembles, in some respects, associations observed in some sedimentary exhalative base-metal deposits (Russell, 1974; Grosdz and Krebs, 1977) and in some sea-floor sediments near possible

**Table 7.** Comparison of abundance of barium, manganese, nickel, cobalt, zinc, lead, and silver in shale and mudstone from western Virginia with the abundances of these elements in the Earth's crust and in some other clays and shales

[Estimates for concentrations in the Earth's crust and for clay, shale, and deep-sea clay are from Parker (1967), who used data from Turekian and Wedepohl (1961) (T & W) and from Vinogradov (1962) (V). In calculation of mean values for Virginia shales, sets of data that contain five or less analyses that were greater or less than the detection limit were calculated by using values of the detection limit and identified with the symbols > (greater than) or < (less than). A dash is shown where more than five analyses were less than or greater than the detection limits and no calculations were made. Data for the Millboro and Needmore Shales are given in tables 2 and 3. All data are in parts per million]

| Elements | In Earth's crust (V) | Clay and shale (V) | Shale (T & W) | Deep-sea clay (T & W) | Millboro Shale | | Needmore Shale | |
|---|---|---|---|---|---|---|---|---|
| | | | | | Barite matrix | No barite | Barite matrix | No barite |
| Barium | 650 | 800 | 580 | 2,300 | >781 | 1,228 | 1,169 | 1,034 |
| Manganese | 1,000 | 670 | 850 | 6,700 | >342 | 99 | 700 | 251 |
| Nickel | 58 | 95 | 68 | 225 | 57 | 24 | 87 | 52 |
| Cobalt | 18 | 20 | 19 | 74 | — | — | — | — |
| Zinc | 83 | 80 | 95 | 165 | — | — | — | — |
| Lead | 16 | 20 | 20 | 80 | <23 | <40 | <20 | <41 |
| Silver | .7 | .1 | .07 | .11 | — | — | — | — |

sources of hydrothermal fluids (Arrhenius and Bonatti, 1965; Bostrom and Peterson, 1966). However, there is little evidence of barium enrichment in shales and mudstones in the vicinity of the barite nodules in western Virginia like that of the barite halos that are associated with bedded barite deposits in Arkansas and Nevada (Brobst, 1984). The composition of shales in the area investigated is similar to that of average clays and shales (table 7). In addition, the shales in the study area do not show any significant enrichment in other elements that would suggest introduction of hydrothermal fluids or brines. A genesis by introduction of barium from submarine springs and subsequent remobilization of the barite fail to account for the consistent association of barite with anaerobic and dysaerobic zones. Although it is certainly possible that submarine springs could have vented into anoxic portions of stratified basins, it seems unlikely that springs would have vented only into anoxic waters. The barite nodules have a wide geographic distribution in rocks of Middle Ordovician to Late Devonian age elsewhere in the Appalachian basin (Clark, 1985, 1986a,b, 1987; Nuelle and Shelton, 1986). The geographic and stratigraphic distribution, along with the consistency of depositional environments, is difficult to explain if submarine springs were the sole source of the barium. Therefore, although it cannot be ruled out that submarine springs introduced barium into anoxic waters of stratified basins to form the nodules, other sources of barium should be considered.

Barite nodules may form peripheral to some bedded barite deposits when barium is remobilized and redeposited during diagenesis (Hanor and Baria, 1977; Hanor, 1982; Cecile and others, 1983). The remobilization of barite from bedded deposits derived from submarine springs has been proposed as a possible origin for the barite nodules of the Appalachian basin (Nuelle and Shelton, 1986). However, no large, bedded deposits have been found that could have provided a source of barium in the nodules.

Derivation of barium from volcanic rocks is possible because of the proximity of the Tioga Ash Bed (fig. 2) to the barite nodule zones in western Virginia. However, the occurrence of barite nodules in other Ordovician to Devonian beds where there are no volcanic rocks in proximity (Clark, 1985, 1986a,b, 1987) makes unlikely the possibility that volcanic rocks are the sole contributor of barium.

If the barium were derived from the redistribution of small amounts of barium in the sedimentary pile, the redistribution process might be reflected in a depletion of barium in the source rocks relative to those where the barite nodules formed. However, the analyses of the barite matrix shales (tables 2 and 3, figs. 10–12) do not a show depletion of barium relative to shales from outside the barite nodule zones.

## Marine Barite

Marine barium that is partly, if not entirely, biogenic can provide an intermediate source of barium. Small amounts of barium introduced into seawater from diverse ultimate sources can be concentrated in marine barite prior to dissolution in anoxic water that is the immediate source of barite in the nodules. Concentration of barium by marine organisms is a well-known process. Bowen (1956) reported barium concentrations ranging from 450 to 4,400 times that of seawater in a variety of marine organisms. Observations by Chow and Goldberg (1960), Arrhenius and Bonatti (1965), Dean and Schreiber (1978), Church (1979), and Schmitz (1987) show that the involvement of organisms can be important in barite formation. Barite nodules have been reported from deep-sea sediments at many localities. Dean and Schreiber (1978) proposed that barite in deep-sea sediments had a diagenetic origin in oxidizing or slightly reducing environments and that the main source of barium was from the oxidation of organic matter. Incorporation of barium from dissolved authigenic marine barite and barium-bearing organic debris into barite concretions has been

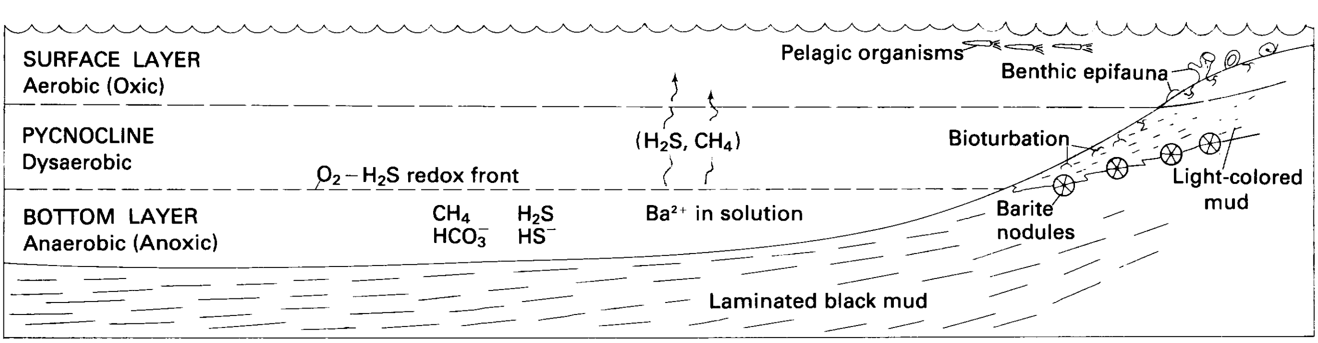

**Figure 15.** Model for the formation of barite nodules in a stratified basin. Depth estimates and relations among degree of oxygenation, biofacies, and lithofacies are adapted from Rhoads and Morse (1971), Byers (1977), Newton (1979), Ettensohn and Barron (1981), and Ettensohn (1985).

described by Bogoch and others (1987) in Eocene chalks in Israel.

## CONCLUSIONS

Barium that is introduced into seawater from dilute sources can be concentrated by marine processes, then dissolved in anoxic bottom waters, and later precipitated at redox interfaces to produce barite nodules. The geologic relations of the barite nodules suggest that the formation of the nodules took place slowly, rather than as the result of rapid introduction of barium into the seawater. A simplified model showing possible relations of barite nodules to redox fronts in a stratified marine basin is shown in figure 15. Barium from oxygenated waters of the surface layer can reach deeper anoxic waters through the marine biologic cycle in the form of waste products and tissues and by adsorption to shell material. Barium would be soluble in the anoxic water, either in anoxic bottom waters or in interstitial pores of the sediment below the sediment-seawater interface. The barium can precipitate as barium sulfate at redox fronts between anoxic waters and the slightly more oxygenated waters of the dysaerobic zone, or pycnocline.

Growth of barite nodules in Devonian shales of western Virginia began in unconsolidated sediments during diagenesis in an environment that had fluctuating chemical conditions. The boundary between anaerobic and dysaerobic facies, as determined by fauna and sedimentary structures, has been preserved by distinctive biofacies, lithofacies, and patterns of distribution of manganese, nickel, cobalt, zinc, lead, and silver. This boundary could have been the location of high concentrations of sulfur-reducing bacteria. The boundary served as a locus for the formation of barite nodules below the sediment-water interface, possibly with microbes serving as a catalyst. The presence of a concentration gradient between barium in solution in anoxic pore waters and more oxygenated sulfate waters may account for the migration of barium toward the boundary in production of local barium concentrations. Barite nodules also formed in anaerobic to dysaerobic zones in association with carbonate nodules and areas of locally increased alkalinity. The local increase in alkalinity in the anaerobic zone could have been the result of bacterial decay of organic matter. The presence of carbonate minerals, which buffer the pH, may have permitted the barite to remain stable under reducing conditions.

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## REFERENCES CITED

Anger, G., Nielsen, H., Puchelt, H., and Ricke, W., 1966, Sulfur isotopes in the Rammelsburg ore deposit (Germany): Economic Geology, v. 61, no. 3, p. 511–536.

Arrhenius, G.F., and Bonatti, E., 1965, Neptunism and vulcanism in the ocean, *in* Sears, M., ed., Progress in Oceanography, v. 3: New York, Pergamon Press, p. 7–22.

Avary, K.L., ed., 1979, Devonian clastics in West Virginia and Maryland: Field Trip Guide, October 3–5, 1979, conducted for Eastern Section, American Association of Petroleum Geologists Meeting, Morgantown, West Virginia, 100 p.

Berner, R.A., 1968, Calcium carbonate concretions formed by the decomposition of organic matter: Science, v. 159, no. 3811, p. 195–197.

Bick, K.F., 1962, Geology of the Williamsville quadrangle, Virginia: Virginia Division of Mineral Resources Report of Investigations 2, 40 p.

Bjorlykke, K.O., and Griffin, W.L., 1973, Barium feldspars in Ordovician sediments, Oslo region, Norway: Journal of Sedimentary Petrology, v. 43, no. 2, p. 461–465.

Blome, C.D., and Albert, N.R., 1985, Carbonate concretions: An ideal sedimentary host for microfossils: Geology, v. 13, no. 3, p. 212–215.

Bogoch, R., Buchbinder, B., and Nielsen, H., 1987, Petrography, geochemistry, and evolution of barite concretions in Eocene pelagic chalks from Israel: Journal of Sedimentary Petrology, v. 57, no. 3, p. 522–529.

Bostrom, K., and Peterson, M.N.A., 1966, Precipitates from hydrothermal exhalations on the East Pacific Rise: Economic Geology, v. 61, no. 7, p. 1258–1265.

Bowen, H.J.M., 1956, Strontium and barium in sea water and marine organisms: United Kingdom, Journal of Marine Biology Association, v. 35, p. 451–460.

Brobst, D.A., 1984, The geological framework of barite resources: Transactions of the Institution of Mining and Metallurgy, Section A, v. 93, p. A123–A130.

Burns, R.G., and Burns, V.M., 1979, Manganese oxides, *in* Burns, R.G., ed., Marine minerals: Mineralogical Society of America Short Course Notes, v. 6, p. 1–46.

Buschendorf, F., Nielsen, H., Puchelt, H., and Ricke, W., 1963, Schwefel-Isotopen-Untersuchungen am Pyrit-Sphalerit-Baryt-Lager Meggen/Lenne (Deutschland) und an verschiedenen Devon-Evaporiten: Geochimica et Cosmochimica Acta, v. 27, no. 5, p. 501–523.

Butts, C., 1940, Geology of the Appalachian Valley in Virginia—Part 1, Geologic text and illustrations: Virginia Geological Survey Bulletin 52, 568 p.

Byers, C.W., 1977, Biofacies patterns in euxinic basins: A general model: Society of Economic Paleontologists and Mineralogists Special Publication 25, p. 5–17.

Cannon, W.F., and Force, E.R., 1983, Potential for high-grade shallow-marine manganese deposits in North America, *in* Shanks, W.C., III, ed., Cameron volume on unconventional mineral deposits: New York, American Institute of Mining, Metallurgical, and Petroleum Engineers, Society of Mining Engineers, p. 175–189.

Cate, A.S., 1963, Lithostratigraphy of some Middle and Upper Devonian rocks in the subsurface of southwestern Pennsylvania, *in* Shepps, V.C., ed., Symposium on Middle and Upper Devonian stratigraphy of Pennsylvania and adjacent States: Pennsylvania Geological Survey, 4th ser., Bulletin G39, p. 229–240.

Cecile, M.P., Shakur, M.A., and Krouse, H.R., 1983, The isotopic composition of western Canadian barites and possible derivation of oceanic sulfate $\delta^{34}S$ and $\delta^{18}O$ age curves: Canadian Journal of Earth Sciences, v. 20, no. 10, p. 1528–1535.

Chow, T.J., and Goldberg, E.D., 1960, On the marine geochemistry of barium: Geochimica et Cosmochimica Acta, v. 20, nos. 3–4, p. 192–198.

Church, T.M., 1970, Marine barite: San Diego, University of California, unpublished Ph.D. dissertation, 133 p.

———1979, Marine barite, *in* Burns, R.G., ed., Marine minerals: Mineralogical Society of America Short Course Notes, v. 6, p. 175–209.

Clark, S.H.B., 1985, Diagenetic barite nodules in Ordovician and Devonian shales of the Appalachian basin: Geological Society of America Abstracts with Programs, v. 17, no. 7, p. 548.

———1986a, Barite concentration from anoxic seawater at reduction-oxidation interfaces in stratified basins: Geological Society of America Abstracts with Programs, v. 18, no. 6, p. 565.

———1986b, The origin of some shale-hosted barite nodules of the Appalachian basin [abs.]: TERRA cognita, v. 6, no. 3, p. 514.

———1987, Zinc, lead, and barium deposits and occurrences in Paleozoic sedimentary rocks, east-central United States: U.S. Geological Survey Miscellaneous Investigations Series Map I–1773, scale 1:2,500,000.

Claypool, G.E., Holser, W.T., Kaplan, I.R., Sakai, H., and Zak, I., 1980, The age curves of sulfur and oxygen isotopes in marine sulfate and their mutual interpretation: Chemical Geology, v. 28, nos. 3–4, p. 199–260.

Cooper, B.N., 1961, Grand Appalachian field excursion: The Virginia Polytechnic Institute Engineering Extension Series Geological Guidebook No. 1, p. 149–150.

Dean, W.E., and Schreiber, B.C., 1978, Authigenic barite, Leg 41 Deep Sea Drilling Project, *in* California University, Scripps Institution of Oceanography, LaJolla, Initial reports of the Deep Sea Drilling Project: v. XLI: Washington, D.C., National Science Foundation, p. 915–931.

Dennison, J.M., 1961, Stratigraphy of Onesquethaw Stage of Devonian in West Virginia and bordering states: West Virginia Geological Survey Bulletin 22, 87 p.

———1971, Petroleum related to Middle and Upper Devonian deltaic facies in central Appalachians: American Association of Petroleum Geologists Bulletin, v. 55, no. 8, p. 1179–1193.

Dennison, J.M., and Head, J.W., 1975, Sea level variations interpreted from the Appalachian basin Silurian and Devonian: American Journal of Science, v. 275, no. 10, p. 1089–1120.

Dennison, J.M., Schwietering, J.F., Avary, K.L., and Hasson, K.O., 1979, Roadlog and stop descriptions, *in* Avary, K.L., ed., Devonian clastics in West Virginia and Maryland: Field Trip Guide, October 3–5, 1979, conducted for Eastern Section, American Association of Petroleum Geologists Meeting, Morgantown, West Virginia, p. 13–64.

Dennison, J.M., and Textoris, D.A., 1977, Stratigraphy and petrology of Devonian shales in Appalachian basin, *in* Schott, G.L., Overbey, W.K., Jr., Hunt, A.E., and Komar, C.A., eds., Proceedings of the first eastern gas shales symposium, October 17–19, 1977, Morgantown, West Virginia: U.S. Department of Energy, Morgantown Energy Research Center, Publication MERC/SP-77/5, p. 166–182.

de Witt, W., Jr., 1974, Geologic map of the Beans Cove and Hyndman quadrangles and part of the Fairhope quadrangle, Bedford County, Pennsylvania: U.S. Geological Survey Miscellaneous Investigations Series Map I–801, scale 1:24,000.

Ettensohn, F.R., 1985, Controls on development of Catskill Delta complex basin-facies, *in* Woodrow, D.L., and Sevon, W.D., eds., The Catskill Delta: Geological Society of America Special Paper 201, p. 65–77.

Ettensohn, F.R., and Barron, L.S., 1981, Depositional model for the Devonian-Mississippian black shales of North America: A paleoclimatic-paleogeographic approach, *in* Roberts, T.G., ed., GSA Cincinnati '81, Field Trip Guidebooks, v. 2: Falls Church, Virginia, American Geological Institute, p. 344–361.

Goddard, E.N., Trask, P.D., DeFord, R.K., Rove, O.N., Singewald, J.T., and Overbeck, R.M., 1948, Rock-color chart: Washington, D.C., National Research Council, 6 p. (Republished by Geological Society of America, 1951; reprinted 1963, 1970, 1975, 1979.)

Grimes, D.J., and Marranzino, A.P., 1968, Direct-current arc and alternating-current spark emission spectrographic field methods for semiquantitative analysis of geologic materials: U.S. Geological Survey Circular 591, 6 p.

Grosdz, W., and Krebs, W., 1977, Manganese halo surrounding Meggen ore deposit, Germany: Transactions of the Institution of Mining and Metallurgy, Sec. B, v. 86, p. B73–B77.

Hanor, J.S., 1982, Problems concerning the geochemistry and genesis of stratiform barite-pyrite ore deposits in Arkansas, *in* McFarland, J.D., III, ed., Contributions to the geology of Arkansas, v. 1: Arkansas Geological Commission, Miscellaneous Publication 18, p. 27–32.

Hanor, J.S., and Baria, L.R., 1977, Controls on the distribution of barite deposits in Arkansas, *in* Stone, C.G., ed., Geology of the Ouachitas, v. 2: Arkansas Geological Commission Symposium on the Ouachita Mountains, p. 42–49.

Jacobs, L., and Emerson, S., 1982, Trace metal solubility in an anoxic fjord: Earth and Planetary Science Letters, v. 60, no. 2, p. 237–252.

Johnson, J.G., Klapper, G., and Sandberg, C.A., 1985, Devonian eustatic fluctuations in Euramerica: Geological Society of America Bulletin, v. 96, no. 5, p. 567–587.

Large, D.E., 1981, Sediment-hosted submarine exhalative lead-zinc deposits—A review of their geological characteristics and genesis, *in* Wolf, K.H., Handbook of strata-bound and stratiform ore deposits: Amsterdam, Elsevier Scientific Publishing Company, pt. 3, v. 9, p. 469–507.

Lesure, F.G., 1957, Geology of the Clifton Forge iron district, Virginia: Virginia Polytechnic Institute Engineering Experiment Station Series Bulletin 118, 130 p.

Mosier, E.L., and Motooka, J.M., 1983, Induction coupled plasma-atomic emission spectrometry—Analysis of subsurface Cambrian carbonate rocks for major, minor, and trace elements, *in* Kisvarsanyi, G., Grant, S.K., Pratt, W.P., and Koenig, J.W., eds., International conference on Mississippi Valley type lead-zinc deposits: Rolla, Missouri, University of Missouri—Rolla, p. 155–165.

Motooka, J.M., and Grimes, D.J., 1976, Analytical precision of one-sixth order using semiquantitative spectrographic analyses: U.S. Geological Survey Circular 738, 25 p.

Murray, J.W., 1975, The interaction of metal ions at the manganese dioxide-solution interface: Geochimica et Cosmochimica Acta, v. 39, no. 4, p. 505–519.

Newton, C.R., 1979, Biofacies patterns in the Needmore Shale: Paleoenvironmental and paleobathymetric implications, *in* Avary, K.L., ed., Devonian clastics in West Virginia and Maryland: Field Trip Guide, October 3–5, 1979, conducted for Eastern Section, American Association of Petroleum Geologists Meeting, Morgantown, West Virginia, p. 77–82.

Nuelle, L.M., and Shelton, K.L., 1986, Geologic and geochemical evidence of possible bedded-barite deposits in Devonian rocks of the Valley and Ridge province, Appalachian Mountains: Economic Geology, v. 81, no. 6, p. 1408–1430.

Oliver, W.A., Jr., de Witt, W., Jr., Dennison, J.M., Hoskins, D.M., and Huddle, J.W., 1968, Devonian of the Appalachian basin, United States, *in* International symposium on the Devonian System, Calgary, 1967, Proceedings, v. 1: Calgary, Alberta, Alberta Society of Petroleum Geologists, p. 1001–1040.

———1969, Correlation of Devonian rock units in the Appalachian basin: U.S. Geological Survey Oil and Gas Investigations Chart OC–64.

Papke, K.G., 1984, Barite in Nevada: Nevada Bureau of Mines and Geology Bulletin 98, 125 p.

Parker, R.L., 1967, Composition of the Earth's crust: U.S. Geological Survey Professional Paper 440–D, p. D1–D19.

Pepper, J.F., Clark, S.H.B., and de Witt, W., Jr., 1985, Nodules of diagenetic barite in Upper Devonian shales of western New York: U.S. Geological Survey Bulletin 1653, 11 p.

Poole, F.G., 1986, Stratiform barite in Paleozoic rocks of the western United States [abs.]: TERRA cognita v. 6, no. 3, p. 516.

Raiswell, R., 1971, The growth of Cambrian and Liassic concretions: Sedimentology, v. 17, p. 147–171.

Revelle, R., and Emery, K.O., 1951, Barite concretions from the ocean floor: Geological Society of America Bulletin, v. 62, p. 707–724.

Rhoads, D.C., and Morse, J.W., 1971, Evolutionary and ecologic significance of oxygen-deficient marine basins: Lethaia, v. 4, p. 413–428.

Russell, M.J., 1974, Manganese halo surrounding the Tynagh ore deposit, Ireland: A preliminary note: Transactions of the Institution of Mining and Metallurgy, Sec. B, v. 83, p. B65–B66.

Rye, R.O., Shawe, D.R., and Poole, F.G., 1978, Stable isotope studies of bedded barite at East Northumberland Canyon in Toquima Range, central Nevada: U.S. Geological Survey Journal of Research, v. 6, no. 2, p. 221–229.

Schmitt, H.H., ed., 1962, Equilibrium diagrams for minerals at low temperature and pressure: Cambridge, Massachusetts, The Geological Club of Harvard, 199 p.

Schmitz, B., 1987, Barium, equatorial high productivity, and the northward wandering of the Indian continent: Paleoceanography, v. 2, no. 1, p. 63–77.

Sorokin, J.I., 1964, On the primary production and bacterial activities in the Black Sea: Journal du Conseil, v. 29, no. 1, p. 41–60.

———1966, On the trophic role of chemosynthesis and bacterial biosynthesis in water bodies, *in* Goldman, C.R., ed., Primary productivity in aquatic environments: Memorie Instituto Italiano di Idiobiologia, 18 Supplement, Berkeley, University of California Press, p. 189–205.

Spencer, D.W., and Brewer, P.G., 1971, Vertical advection, diffusion, and redox potentials as controls on the distribution of manganese and other trace metals dissolved in waters of the Black Sea: Journal of Geophysical Research, v. 76, no. 24, p. 5877–5892.

Turekian, K.K., and Wedepohl, K.H., 1961, Distribution of the elements in some major units of the earth's crust: Geological Society of America Bulletin, v. 72, no. 2, p. 175–192.

Vinogradov, A.P., 1962, Average contents of chemical elements in the principal types of igneous rocks of the earth's crust: Geokhimiya, no. 7, p. 555–571 [in Russian]; translation to English in Geochemistry, no. 7, p. 641–664.

Way, J.H., and Smith, R.C., II, 1983, Barite in the Devonian Marcellus Formation, Montour County: Pennsylvania Geology, v. 14, no. 1, p. 4–9.

Weeks, L.G., 1953, Environment and mode of origin and facies relationships of carbonate concretions in shales: Journal of Sedimentary Petrology: v. 23, no. 3, p. 162–173.

Woodward, H.P., 1932, Geology and mineral resources of the Roanoke area, Virginia: Virginia Geological Survey Bulletin 34, 172 p.

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