Geologic, Geochemical, and Isotopic Studies of a Carbonate- and Siliciclastic-Hosted Pb-Zn Deposit at Lion Hill, Vermont

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U.S. DEPARTMENT OF THE INTERIOR

MARCH 3, 1849

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A study of Pb-Zn-Cu mineralization resulting from syngenetic sedimentary-exhalative and diagenetic replacement processes in structures in carbonate and siliciclastic platform rocks of Cambrian and Ordovician age that form the lowlands between the Green Mountain massif and the Adirondack massif in western Vermont

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GEOLOGIC, GEOCHEMICAL, AND ISOTOPIC STUDIES OF A CARBONATE- AND SILICICLASTIC-HOSTED Pb-Zn DEPOSIT AT LION HILL, VERMONT

By Nora K. Foley,[1] Sandra H.B. Clark,[1] Laurel G. Woodruff,[2] and Elwin L. Mosier[3]

ABSTRACT

Zn-, Pb-, Cu-, and Fe-bearing rocks of the Lion Hill area in western Vermont formed during the Early Cambrian by syngenetic sedimentary-exhalative and diagenetic replacement processes. Sphalerite, galena, chalcopyrite, pyrite, and, locally, magnetite form stratabound and broadly stratiform lenticular zones, ~300 meters long and 25–50 meters thick, which are uneconomic at the present time. The lenses are structurally disrupted and metamorphosed to greenschist facies, probably due to the Taconic orogeny. Textural evidence suggests that mineralizing fluids permeated the sediments prior to lithification and that a dilatant fracture zone, possibly a feeder zone, contains some of the discordant veins at Lion Hill. The veins may have formed when the sediments were in a plastic, semiconsolidated state. The association of layered iron formation containing base-metal sulfide minerals provides possible lithologic evidence for syngenetic mineralization by submarine exhalative activity. Sand bars and tidal channels present in the sedimentary section could have acted as permeable pathways for movement of mineralizing fluids. The complex interlayering in the sedimentary sequence of carbonate and siliciclastic rock types having widely varying permeabilities created numerous fluid traps.

Homogenization temperatures of primary and secondary inclusions in vein sphalerite range from 152°C to 196°C; salinities range from 11.5 to 14.0 equivalent weight percent NaCl. $\delta^{34}S$ values of sulfides from Lion Hill vary from −25.9 to +10.0 per mil, and fall within the expected range for sulfide produced from bacteriogenic reduction of sulfate with $\delta^{34}S$ values of 25 to 30 per mil. In addition, some pyrite probably formed from sulfate in trapped pore fluid that resulted in heavier isotopic values characteristic of more closed-system behavior. Three sphalerite samples that have heavier sulfur isotopic values may reflect a change in the source of sulfur during a later episode of mineralization, perhaps a change to a deep-seated source. Lead isotopic compositions of galenas from mineralized zones at Lion Hill range from 18.351 to 18.632 for $^{206}Pb/^{204}Pb$, from 15.546 to 15.618 for $^{207}Pb/^{204}Pb$, and from 38.126 to 38.496 for $^{208}Pb/^{204}Pb$. The lead isotopic compositions of galena from Lion Hill and fluid inclusion and sulfur isotopic values for the Lion Hill sulfides are more like those of Pb-Zn-Ag deposits of Ireland than those of MVT or Appalachian-type Zn deposits.

The prospect of an Irish-type sedimentary-exhalative origin for stratabound Pb-Zn deposits of the Paleozoic shelf of North America is of considerable importance to understanding the timing of mineralization relative to platform evolution and for evaluating the mineral resource potential of the region. Our study of the Lion Hill deposit indicates a potential for Irish-type Pb-Zn deposits in platform rocks of western Vermont; however, at Lion Hill they contain enrichments of Pb, Zn, and Cu rather than a Pb, Zn, and Ag association.

INTRODUCTION

Base-metal sulfide deposits and occurrences are exposed throughout an area approximately 300 km in length by 90 km in width of carbonate-siliciclastic platform rocks of Cambrian and Ordovician age that form the lowlands between the Green Mountain massif and the Adirondack massif in western Vermont (fig. 1). Lower Cambrian Monkton Quartzite (Cady, 1945) is the host for the largest stratabound Zn-Pb-Cu sulfide zones found at Lion Hill, 3–4 km north of the town of Brandon, Vt., (fig. 1); lesser amounts of base-metal sulfide minerals occur in Winooski Dolomite. In other areas of the western Vermont lowlands (fig. 1), Zn-, Pb-, Fe-, and Cu-sulfide occurrences are found in carbonate-siliciclastic platform rocks of the Danby Formation (at Hinesburg, Vt.) and the Dunham Dolomite (at Fernville, Milton, and Zion Mountain, Vt., and at Dunham, Quebec) (figs. 1 and 3). Lower Cambrian clastics of the

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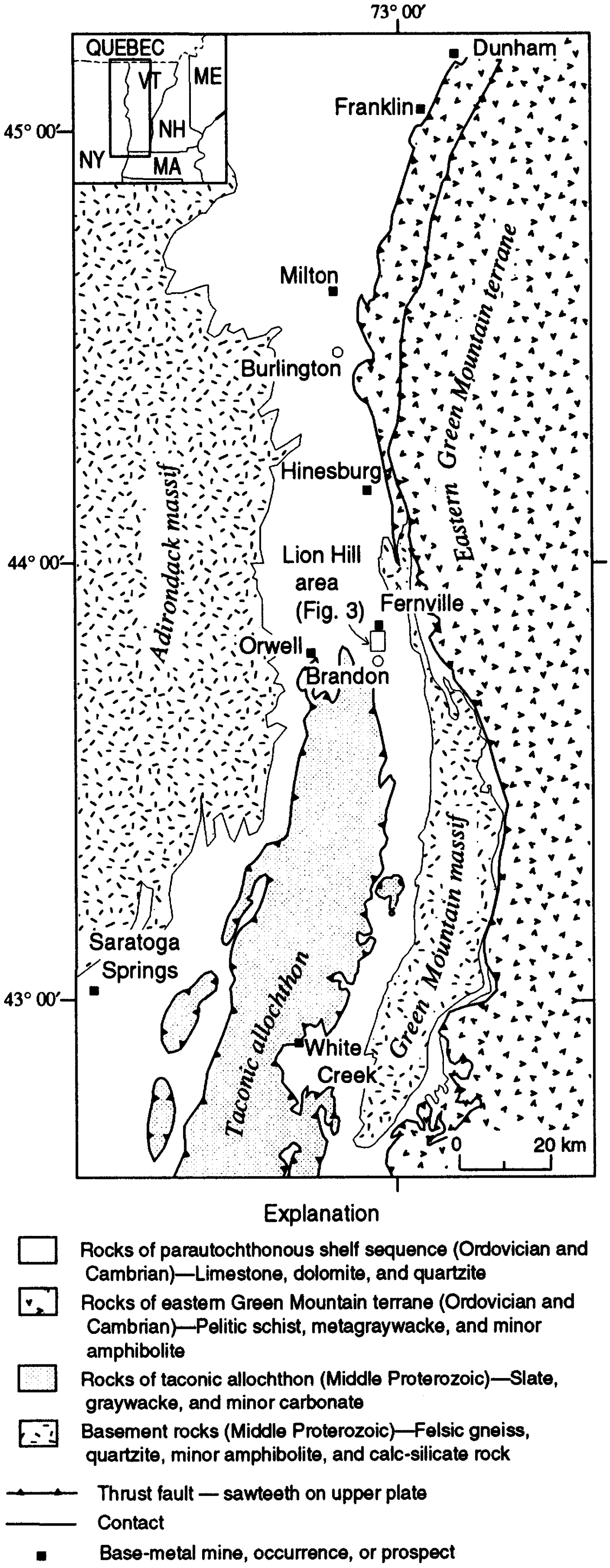

Figure 1. Regional geologic setting of base-metal sulfide deposits and occurrences in Cambrian and Ordovician siliciclastic platform rocks of western Vermont. The Lion Hill area is located just north of the town of Brandon, Vt., and includes the Churchill prospect and Fay and Nicklaw mines. Geologic map modified from Stanley and Ratcliffe (1983, 1985) and Thompson (1990). Other mineralized localities include Dunham, Quebec (Gauthier and others, 1985, 1989; Boucher, 1986), and Orwell, Vt., and Saratoga Springs, N.Y. (Summarized in Clark and Slack, 1988; Clark, 1990; USGS Mineral Resource Data System; N.M. Ratcliffe and S.H.B. Clark, unpub. data, 1990).

Nassau Formation host Zn-Pb-Cu sulfide mineralized rock at White Creek in southern Vermont (Slack and others, 1987; Slack, 1990). Along the eastern side of the Green Mountains, small stratabound deposits of magnetite and hematite and siderite and pyrrhotite are found. These occurrences are contained in pelitic schist, metagraywacke, and minor amphibolite that make up the metamorphic cover sequence of the eastern Green Mountains (Slack and Schruben, 1990; Thompson, 1990).

Most of the occurrences at Lion Hill are small and lack detailed production records. The earliest published reports of the area include mention of a shaft sunk in the 1870's from which ore was apparently mined and a core drilling program headed by St. Joseph Lead Company in 1941. The New Jersey Zinc Company carried out exploration work at Lion Hill from 1952 to 1954; during that time they mapped the Fay shaft, conducted soil sampling, and drilled 30 holes, some of which were ~240 m in depth. The Labradex Corporation conducted an exploratory drilling program of the area including the Fay mine, Churchill Prospect, and Nicklaw mine between 1981 and 1982; they drilled eight holes, one to a depth of 125 m. Studies of these materials provide information upon which some of this report is based. A dominantly synsedimentary origin was proposed for the Zn-Pb (±Cu) mineralized rock occurring in platform rocks at Lion Hill (fig. 1) as the result of a U.S. Geological Survey mineral resource study of the Glens Falls 1° × 2° quadrangle (Clark, 1987; Clark and Slack, 1988; Clark, 1990; Slack, 1990; Foley, 1990). The present study characterizes in more detail the nature and origin of the Lion Hill deposit, including a consideration of the sedimentary environment, petrographic relations of sulfide minerals to sedimentary and deformational fabrics, geochemical signatures of mineralized and unmineralized samples, sulfur and lead isotopic geochemistry, and fluid inclusion thermometry studies. Interpretation of the mineralized rock in the Lion Hill area as a metamorphosed Irish-type sedimentary-exhalative Pb-Zn deposit suggested a potential for commercially important sediment-hosted base-metal-Ag deposits in similar carbonate-siliciclastic shelf sequences that occur throughout western Vermont, eastern New York, northwestern Massachusetts, and southeastern Quebec (Clark, 1990).

ACKNOWLEDGMENTS

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GEOLOGIC SETTING

REGIONAL TECTONIC, SEDIMENTARY, AND METAMORPHIC ENVIRONMENT

Rocks of the Cambrian and Ordovician carbonate-siliciclastic platform were deposited on a shelf that formed the eastern margin of the North American continent following Late Proterozoic rifting (Thompson, 1990). The platform rocks rest unconformably over rocks of the Adirondack basement, which are part of the billion-year-old Grenville terrane that forms much of the southeast part of the North American craton. The carbonate siliciclastic shelf was downfaulted on its eastern margin, and deep-water environments that formed due to opening of the proto-Atlantic Ocean (Iapetus) lay farther to the east. The stratigraphic succession that unconformably overlies Grenville basement begins with basal clastics of Late Proterozoic age to earliest Cambrian age (summarized in Thompson, 1990) that are succeeded in turn by the Cambrian sedimentary rocks. On the developing shelf margin, Cambrian sediments were deposited in a shallow sea; their compositions alternated between dominantly siliciclastic and dominantly carbonate facies (the stratigraphic section from base to top includes the Cheshire Quartzite, Dunham Dolomite, Monkton Quartzite, Winooski Dolomite, and Danby Formation) (Mehrtens, 1985). The terrigenous component was supplied to the sedimentary pile by a land mass located to the west of the platform in the vicinity of the present-day Adirondack Mountains. The lower units (Cheshire and Dunham) are not found to the west, probably due to westerly sedimentary onlap in Early Cambrian time (Zen, 1967). There is no evidence for volcanic rocks locally in the parautochthonous shelf sequence.

Thrusting of deep-water sediments over the shallow-water platform sequence commenced in the Middle Ordovician as part of the Taconic orogeny when the continent collided with an island arc located to the east of the deep-water trench (Zen, 1972). The collision caused rocks of the shelf sequence to collapse and the development of mainly high-angle longitudinal faults (Zen, 1972). The fault movement was accompanied by minor volcanic eruptions (Thompson, 1990). The continental shelf was downfaulted into a deep-water basinal environment of the proto-Atlantic to the east (Friedman, 1979). Sediments that originated on the continental slope were thrust over the platform to form the Taconic allochthon, and the underlying parautohthonous carbonate-siliciclastic platform was deformed into foreland folds (fig. 1). Mineralized rocks of the Lion Hill area are located in the overturned eastern limb of the south-plunging Middlebury synclinorium, a foreland fold that is strongly overturned to the west.

The northern Appalachian region, including southeastern New York, Connecticut, Massachusetts, and Vermont, was subjected to medium-pressure regional metamorphism during the Taconic orogeny at about 450 Ma (Zen, 1967, 1972). Metasedimentary rocks in the vicinity of Lion Hill contain chlorite, epidote, and, locally, rare, pale-green to green-brown biotite (Cady, 1945; Clark, 1990), indicating greenschist facies conditions. Pyrophyllite is not present in the pelitic rocks (Zen, 1960), and the limestones and dolomites do not contain talc, wollastonite, graphite, or other minerals that form by decarbonation reactions; the dolomites show only minor recrystallization. There is no evidence in the area for Acadian deformation (Sutter and others, 1985).

LOCAL TECTONIC, SEDIMENTARY, AND DEFORMATIONAL ENVIRONMENT

Lithofacies and environments of deposition of Monkton Quartzite have been studied in detail in the Burlington, Vt., area (fig. 1). Sedimentary features, such as ripple marks, mud cracks, rain-drop impressions, cross bedding, and trace fossils, are well preserved in the rocks, and Rahmanian (1981a,b) and Mehrtens (1985) have recognized seven lithofacies, each consisting of varying amounts of carbonate and siliciclastic rock. The textures and lithologic cycles led them to propose that the shallowing-upward siliciclastic and siliciclastic-carbonate cycles were characterized by repeated depositional sequences of (1) subtidal siliciclastic sand shoals and channels, (2) interbedded siliciclastic sand, silt, and carbonate intertidal zone sediments, and (3) carbonate mud of the high intertidal to supratidal zone. These supratidal, intertidal, and shallow subtidal sediments interfinger with, and grade into, subtidal oolitic dolostone and platform margin breccias (Mehrtens, 1985). The rocks at Lion Hill and at Burlington are lithologically similar and, hence, probably formed in similar environments, although the Monkton Quartzite at Lion Hill contains a greater proportion of carbonate rocks (metadolostone, arenaceous and phyllitic dolostone) and lesser amounts of siliciclastic rocks than Monkton Quartzite at Burlington.

Deformation and metamorphism have obliterated most sedimentary features in rocks at Lion Hill; however, the lithologies and some rare preserved features support the suggestion that sedimentation was mostly in a shallow-water tidal-flat environment. Some of the rocks show fine color laminations, while others have a mottled appearance. The common occurrence of mottled reddish colors (pale to dark gray, pale orange, pink, orange-pink, and pale red in hue) and the presence of a terrigenous component suggest deposition in an intertidal zone. Admixing of carbonate and siliciclastic materials characterizes much of the Lion Hill section; in some samples, 1- to 2-mm-wide quartz grains appear to float in dolomite. The depositional environment for this rock may be analogous to that which formed intertidal mud-flat deposits in Monkton Quartzite in northwestern Vermont (Mehrtens, 1985). Possible algal fabrics, including laminar and small fingerlike structures and calcite-filled birds-eye (fenestrae) vugs, also are preserved locally in drillcore (fig. 2*A*). These fabrics suggest that intertidal to supratidal facies of deposition and evaporitic conditions could be a part of the depositional environment of Monkton Quartzite at Lion Hill (fig. 2*A*). Although there is no original textural evidence of evaporite conditions in the Monkton Quartzite, some features suggestive of an evaporite-bearing depositional sequence (basal quartzite overlain by metadolostone) indicate at least partial transition from shallow-water clastic to chemical sedimentation. Similar features, combined with fluid-inclusion data, have been used to postulate the occurrence of Silurian evaporites in southeastern Vermont, just south-east of Chester dome (Rich, 1979).

Discontinuous layers of metasandstone are common in Monkton Quartzite at Lion Hill. In drillcore, the layers have medium-scale cross stratification and are characterized by sharp erosional bases and a transition upward into finely laminated material with clay drapes (fig. 2*B*). The textures suggest deposition in a tide-dominated environment, possibly a tidal channel or sand bar in the intertidal zone. A distinctive unit in Monkton Quartzite at Lion Hill is a discontinuous 10- to 20-m-thick metasandstone to quartzite that generally occurs about 50 m below the contact of Monkton Quartzite with Winooski Dolomite. The unit (informally referred to as Ethan Allen quartzite in New Jersey Zinc Company reports) is pale gray, medium- to coarse-grained, and well sorted, and is similar to a coarse-grained, well-sorted, cross-stratified siliciclastic unit in Monkton Quartzite in the Burlington area that Speyer (1983) proposed formed as a sand bar.

Folds in rocks of the Lion Hill area formed predominantly by flexural slip (Burt, 1982). The folds have axes that trend about 10° west of north and plunge about 20° southeast; their axial surfaces dip about 50° to 60° to the east. The overturned Lion Hill anticline, a dominant structure, is representative of this style of folding (fig. 3). Numerous smaller scale folds that occur on its limbs include broad, open, and cylindrical similar folds found in competent strata and isoclinal folds that formed in calcareous rocks and near zones of shearing (Clark, 1990) (fig. 2*C*, *D*). Two stages of deformation of the rocks at Lion Hill are

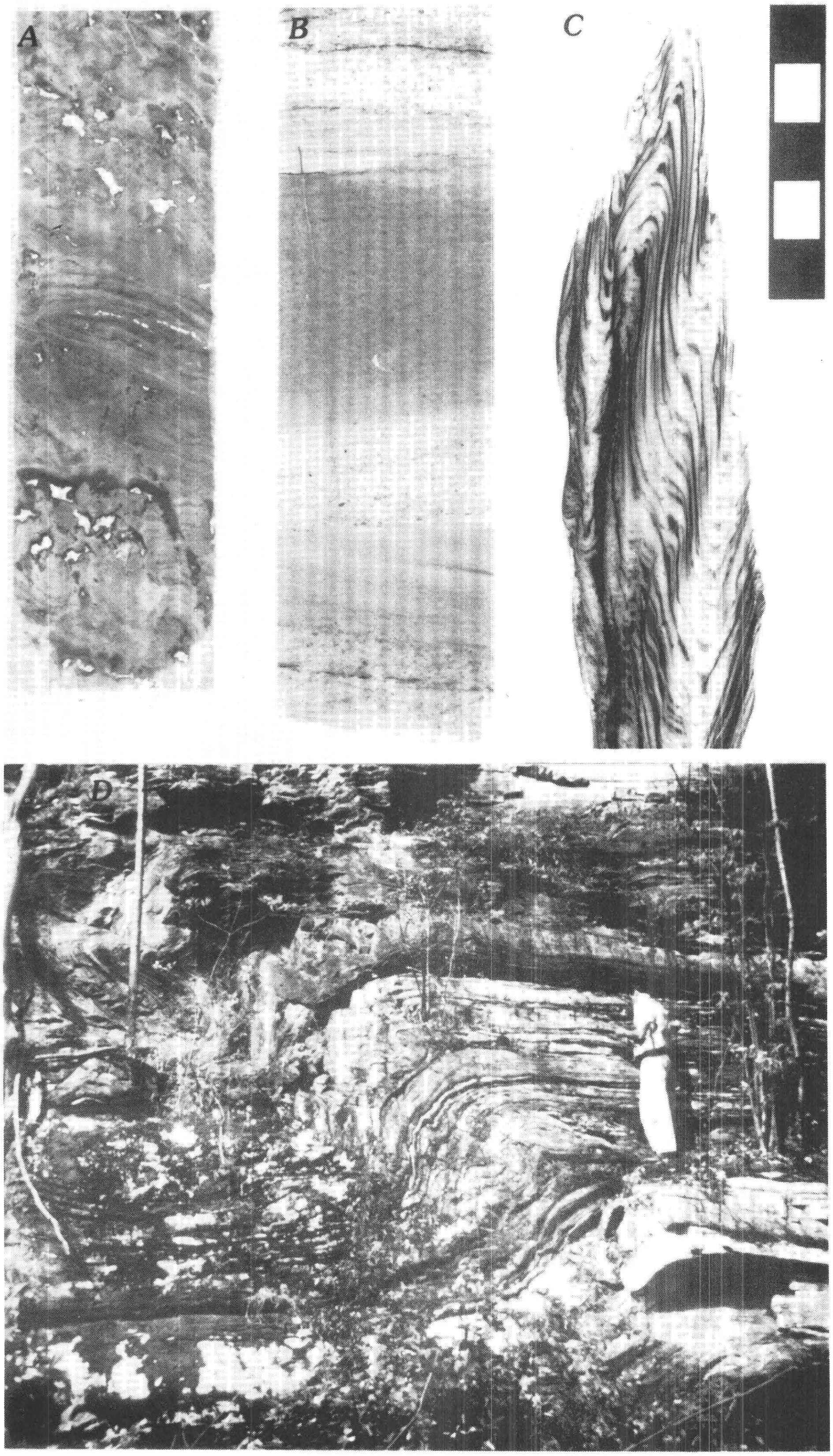


Figure 2. Rocks characteristic of the Lion Hill area. Scale in centimeters. *A*, Probable algal fabrics and calcite-filled fenestrae vugs (white) in dolostone from the Monkton Quartzite at Lion Hill (core L6 at a depth of 38 m). *B*, Medium-scale cross stratification in calcareous metasandstone from the Monkton Quartzite at Lion Hill (core L2 at a depth of 32 m). *C*, Sheared isoclinal folds in metadolostone and phyllite (core L3 at a depth of 7 m). *D*, Outcrop showing large-scale folding.

indicated because the pervasive schistosity (S_1) that developed parallel to compositional layering is itself folded by a second schistosity (S_2) that is parallel to the axial planes of F_2 folds. Sulfide minerals commonly occur along both S_1 and S_2, and sphalerite layers that occur along S_1 are folded by S_2; this folding indicates that some mineralization was syntectonic or pretectonic. The Richmond fault, a high-angle reverse fault, displaces bedding and contacts at Lion Hill (fig. 3) (Clark, 1990). The primary evidence for this fault is stratigraphic offset and the presence of brecciated zones and deformed phyllites in drillcore.

The thickness of the Monkton Quartzite increases abruptly at Lion Hill in the vicinity of the mineralized zones (fig. 3). At Brandon, the Monkton Quartzite is estimated to be about 60 m thick, but at Lion Hill the thickness is between 150 and 180 m (New Jersey Zinc Company, unpub. reports, 1952–54). Lithologic sequences differ dramatically from core to core as a result of both discontinuous sedimentation in a tidal-flat environment (abrupt and irregular facies changes) and superimposed structural complexities (folds, shearing along axial surfaces, and faulting related to development of the foreland folds). The irregularity of patterns can be attributed to original features of tidal-flat deposition, tectonic instability at the time of mineralization, disruptions by Taconic folds and faults, or the effects of a combination of these factors. For example, dolostone breccias are found locally in drillcore, and while some may have formed as intraformational breccias (possible rip-up textures), other breccias clearly formed by dissolution. The apparent increase in stratigraphic thickness could be accounted for by facies control if the facies boundaries are not planar but are irregular and units are facies controlled (units are not necessarily of the same thickness). The apparent thickening also may be accounted for by folding during the Taconic orogeny. Synsedimentary faulting and subsidence could perhaps have resulted in the development of a local basin in which a thicker sequence of Monkton Quartzite was deposited; however, the tidal-flat environment would likely have been destroyed. Evidence for sedimentary breccias in Monkton Quartzite at Burlington and at Lion Hill may indicate some local synsedimentary faulting.

LION HILL Zn-Pb-Cu DEPOSIT

SHAPE AND EXTENT OF MINERALIZED ZONES

The Churchill Prospect (northern ore body) is located in the northern portion of the Lion Hill area on the overturned limb of the Lion Hill anticline (figs. 3, 4*A*). Sulfides occur in a stratabound zone ~10–25 m stratigraphically below the contact of the Monkton Quartzite with the overlying Winooski Dolomite (Clark, 1990). A small mineralized zone occurs near the Nicklaw mine on the upright limb of the Lion Hill anticline 300 m northeast of the Churchill prospect. Sulfides are found approximately 30 m below the contact and may be a continuation of the northern ore body (Churchill Prospect) (figs. 3, 4*A*). Sulfides also are found in the southern part of the Lion Hill area at the Fay (or Oram) mine (figs. 3, 4*B*). The southern mineralized zone is on the upright limb of the Lion Hill anticline. The southern zone occurs in the interval of ~40–60 m below the contact between the Monkton Quartzite and Winooski Dolomite.

The mineralized zones are stratiform and lenticular in overall form but irregular and discontinuous on a local scale (fig. 4*A*, *B*). Small clots and discontinuous stringers of Zn, Pb, and Cu sulfides also occur in rocks above and below the main sulfide bodies, in Monkton Quartzite and Winooski Dolomite. Gray metadolostone is the most common host rock for Zn-, Pb- and Cu-sulfide minerals, although they also occur in metasandstone and phyllite. Zones delineated by mining company personnel for both areas have fairly restricted thicknesses (15–60 m). Small- to large-scale tight folds seen in surface exposures and in samples of core appear to die out within short distances in alternating layers of metadolostone, phyllite, and quartzite. The structures shown in drillcore (fig. 2) mirror fold styles that are exposed in the shaft and drifts in the Fay mine. The sulfide minerals occur as metamorphic segregations along schistosity or shear surfaces parallel to bedding, stringers in matrix-supported dolostone breccia, intergranular sulfides in cross-stratified metasandstone, fillings in discordant fractures and veins, and layered sulfide-bearing magnetite iron formation.

HOST ROCKS

The predominant rock types in the Lion Hill area are arenaceous metadolostone, metasandstone, and phyllite. Distinctions between rock types generally are gradational, and individual units consist of varying proportions of these three rock types.

In general, dolomite comprises 50 to 60 volume percent of the metadolostones; the rest of the rock is composed of quartz, K-feldspar, sericite, muscovite, and biotite intergrown with chlorite. Accessory minerals include pyrite, zircon, leucoxene, magnetite, ilmenite, and tourmaline. These commonly are rounded and occur with the micaceous minerals in phyllitic layers or are segregated into irregularly shaped dark layers. This segregation originally may have formed by bioturbation. Some parts of the metadolostones are composed almost entirely of a fine mosaic of dolomite grains with less than 5 percent accessory quartz, K-feldspar, and sericite. Isolated cubes of pyrite also occur in the metadolostones; deformed shapes and pressure shadows indicate pretectonic to syntectonic crystallization. Locally in the dolomite, breccia zones containing angular fragments occur that are probably tectonic in origin, although some could be dissolution features. Coarse-grained, pale-gray dolomite

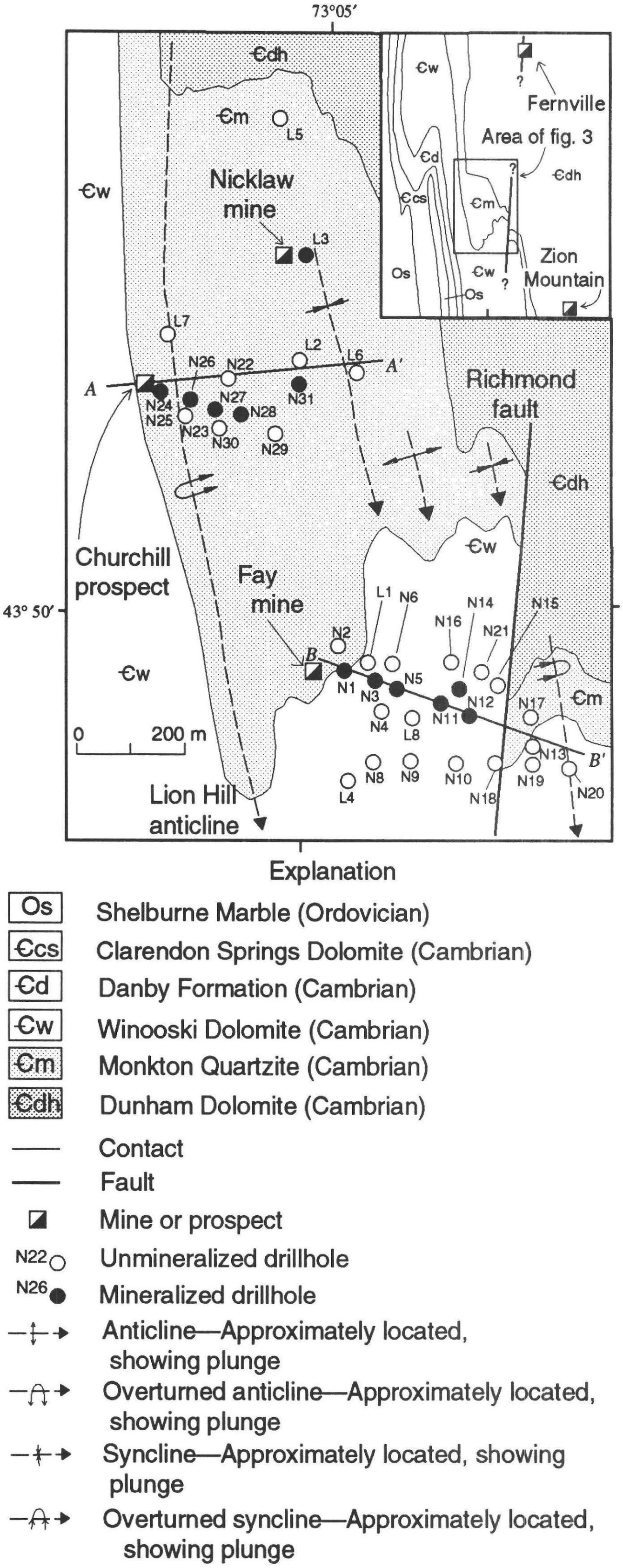


Figure 3. Geology of the Brandon area, modified from Cady (1945) and Burt (1982). Inset map shows local geologic setting. Locations of drillholes (closed circles identify holes that intersect an ore body; open circles represent holes that intersect weakly mineralized or unmineralized rock) and mine workings are given.

and quartz fill the spaces between clasts in unmineralized breccias. In mineralized zones, sphalerite, galena, and chalcopyrite form the matrix of dolomite breccias.

Phyllitic, dolomitic metasandstone is common in both Monkton Quartzite and Winooski Dolomite at Lion Hill. Grain sizes range from fine to coarse in some rocks, but a bimodal distribution is also common, with larger clasts of predominantly subangular to subrounded quartz and K-feldspar set in a finer grained matrix. The matrix material is composed of quartz, K-feldspar, mica, and carbonate. Potassium feldspar is a common constituent of the rocks, making up from 5 to 35 percent of the metasandstones. Micaceous minerals (sericite, muscovite, and fine-grained, pale-green and greenish-brown biotite) make up as much as 35 percent of some of the metasandstones. Dolomite occurs both as fragments and as fine-grained material in the matrix. Accessory minerals include zircon, rutile, sphene, epidote, pyrite, tourmaline, and leucoxene (some with magnetite or ilmenite cores); these minerals are subrounded and probably are detrital in origin. Concentrations of leucoxene and rutile parallel to bedding, as defined by grain-size variations, suggest mechanical concentration during sedimentation. Tourmaline occurs in small amounts (<1 percent), most commonly as rounded green grains that may have brown overgrowths. The alignment of brown euhedral grains of tourmaline in the plane of the schistosity suggests that tourmaline also grew during metamorphism.

Arenaceous and dolomitic varieties of phyllite contain the same minerals as the metadolostones and metasandstones but have greater than 50 percent micaceous minerals and lesser amounts of quartz, feldspar, and dolomite. Effects of metamorphism, while evident in other rock types, are especially well developed in the phyllites. Schistosity and foliation are defined by orientation and segregation of micaceous minerals, elongation and recrystallization of quartz grains, and cataclastic flow features. Rotational snowball textures are seen in some grains, and micaceous layers curve around large clasts of quartz. Recrystallized pyrite forms euhedral crystals (0.5 cm) in some phyllites and is spatially associated with possible algal structures (in dolomitic phyllite). The pyrite may be diagenetic (for example, recrystallized framboidal pyrite) and may reflect the former presence of organic matter that decomposed under reducing conditions in the sediments.

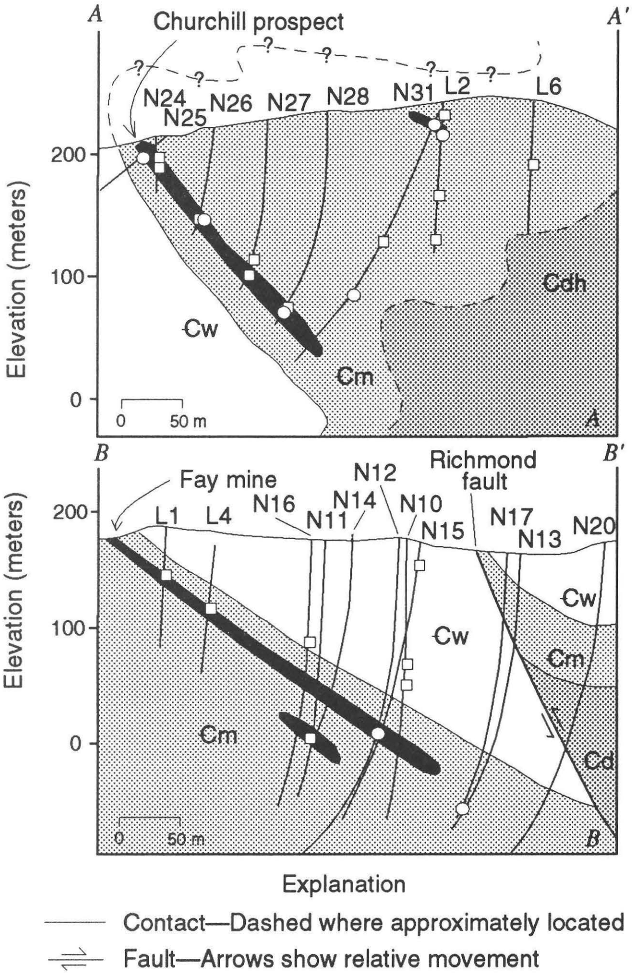


Figure 4. Cross sections along lines *A–A'* and *B–B'* of figure 3 showing mineralized zones (shaded) and sample locations: open squares locate samples used in sulfur isotopic study; open circles locate samples for lead isotopic study. Dashed line in 4*A* indicates possible fold geometry based on surface geology. Surface intersections of drillholes are labeled (for example, N12); holes are located on figure 3. Prepared from Cady (1945), New Jersey Zinc Company (unpub. data, 1952–54), Labradex Corporation (unpub. data, 1982), and Clark (1990). See figure 3 for explanation of geologic map units.

MINERALIZED ROCKS

Mineralized rocks at Lion Hill are primarily fine-grained, massive pale-gray metadolostone and locally dark-gray phyllite that contain stringers and small irregular masses of fine-grained sphalerite, galena, pyrite, and chalcopyrite (in decreasing order of abundance). Textures of the mineralized rocks can be grouped into four types: metamorphic segregations, intergranular fillings, layered sulfides, and discordant veins with open-space fillings. The effects of metamorphism and deformation have obliterated most primary fabrics; however, premetamorphic features including sulfides filling intergranular spaces in dolomite and layered magnetite iron formation are preserved in some places. Pyrite occurs as inclusions and irregular grains intergrown with other sulfide minerals in mineralized horizons and also forms cubes that are widespread in unmineralized and mineralized sedimentary rocks.

Metamorphic segregations are the most common sulfide occurrence. Sphalerite, galena, and chalcopyrite typically occur in discontinuous layers that are elongate within schistosity and shear planes (figs. 5*A* and 6*A*). In the metamorphic segregations, sphalerite and galena are intergrown with quartz, carbonate, microcline, and schistose biotite and chlorite. Minerals in the segregations are coarser grained than those in the host rocks, reflecting mobilization and recrystallization during metamorphism.

Pale-brown sphalerite fills spaces between dolomite grains and is concentrated along bedding planes, including cross stratification (fig. 5*C*). Sphalerite appears to completely permeate the rock and forms intergranular cementing material. In thin section, irregularly shaped, unzoned, yellow intergranular sphalerite fills spaces between dolomite and quartz grains of the host rocks and is concentrated along coarser grained basal portions of graded beds (fig. 6*B*). The intergranular sulfide minerals are interpreted to have formed as the result of diagenetic introduction of metal-bearing fluids into the rocks. Pale-brown sphalerite, galena, and chalcopyrite that form the matrix of breccias (fig. 5*B*) also may have originated as diagenetic minerals, like the interstitial sphalerite. The sulfide minerals and carbonate fragments show evidence of recrystallization at contacts.

Large pieces of layered magnetite iron formation consisting of finely laminated magnetite concentrated in layers about 2 to 3 cm thick (fig. 5*F*) are found in dumps near the Nicklaw mine. Disseminated accessory magnetite grains also occur in sulfide-rich stringers in drillcore, but samples having magnetite-rich layers have been observed only in the dump material. Iron formation has not been found in outcrop or drillcore from elsewhere in the area, but the size, abundance, and location of the pieces on a mine dump at the top of Lion Hill indicate that they probably were taken out of the mine. In addition to magnetite, iron formation contains brown sphalerite and chalcopyrite, minor pyrite and galena, and traces of specular hematite. Both galena and pyrite occur as inclusions in magnetite (fig. 6*C*) and as separate grains. Magnetite and sulfide minerals are interlayered with quartz, quartz-carbonate, or biotite-chlorite-bearing bands. A strong schistosity is developed in the micaceous minerals, and euhedral grain borders commonly are present in the magnetite grains. The presence of base-metal sulfides in the iron formation, especially inclusions of galena in magnetite that are isotopically like galena in other textures, further supports that the iron formation is related to mineralization in the Lion Hill area.

Base-metal sulfide minerals also occur as discordant veins or irregular masses that cut bedding of the host rocks. The material filling the fracture cuts across bedding and, in turn, is cut by schistosity. For example, one small fracture preserved in drillcore is filled with carbonate and silicate grains like those of the surrounding rock and includes traces of sphalerite (fig. 5*D*). This texture suggests that material flowed into the fracture when the rock was in a semilithified state. More commonly, discordant veins cut obviously brittle host rocks, and quartz, dolomite, and microcline form thin borders between the host rock and the sulfide minerals. The textures of these veins may result from the reaction of hot, saline, water-rich fluids with carbonate wallrock in a feeder zone and by the movement of fluids through dilatant fracture zones in semilithified sediments.

Other veins are composed entirely of sulfide minerals and cut both host rocks and early calcite-cemented solution breccia (fig. 5*E*). Euhedral quartz crystals line some veinlets, clearly indicating the presence of open space locally during at least one period of crystallization. These veins may represent either (1) local areas of late-stage mineralization that were not deformed during the Taconic orogeny, (2) veins formed by post-peak metamorphic crystallization, or (3) an entirely separate mineralizing event. Cross-cutting veins and blebs of gangue minerals (quartz, calcite, and microcline) occur sparsely in areas outside the mineralized zones, in addition to being associated with sulfide minerals in some veins.

GEOCHEMISTRY

GEOCHEMICAL DATA

Lithologic logs and inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analyses for 9 of the 38 drillholes (see appendix A) illustrate characteristic element distribution patterns for sections that contain established mineralized zones (N26, N28, N11, N14; shaded zone on fig. 7*A*, *B*, *E*, and *F*) and for sections that are weakly mineralized or unmineralized (L2, L3, L6, N10, N13; fig. 7*C*, *D*, *G*, *H*, *I*). For the purposes of this study, a weakly mineralized or unmineralized section is one that lacks a mineralized zone as delineated by mining company personnel, based on a combination of factors including proportion of sulfide minerals to wallrock, thickness of mineralized zone, and ore grades. Elements that show a systematic relationship to the mineralized zones based on ICP-AES analyses are Zn, Pb, Cu, Ag, Cd, and As. In the most intensely mineralized zones, Co, Ni, Mo, Sb, and W also are present in anomalous amounts relative to unmineralized and weakly mineralized zones (table 1). No conclusive geochemical patterns related to mineralization were detected for any other elements analyzed for the study.

Lithologies and geochemical data for individual drillholes in the Lion Hill area are given in figure 7. Drillholes N26 and N28 (fig. 7*A*, *B*) intersect the Churchill prospect (northern mineralized zone) in an overturned section of Monkton Quartzite (figs. 3, 4*A*). Cores L2 and L6 (figs. 7*C*, *D*) are from holes drilled east of the Churchill prospect (fig. 4*A*); L2 intersects a small weakly mineralized zone on the upper limb of the overturned syncline, and L6 penetrates weakly mineralized and unmineralized rock east of the mineralized zone. Cores N11 and N14 (fig. 7*E*, *F*) are from drillholes that intersect the Fay mine sulfide lens (southern mineralized zone) in an upright section of

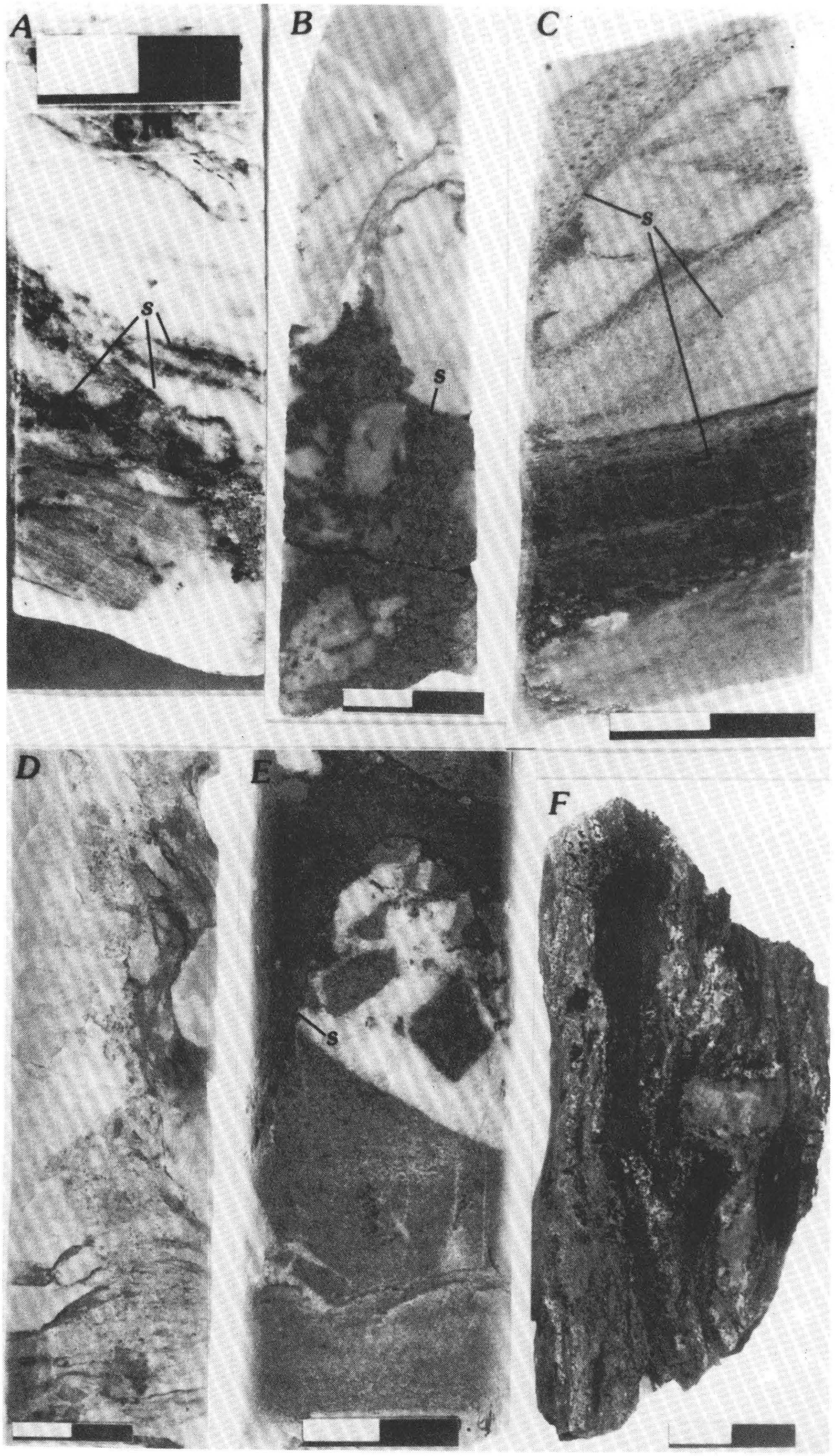


Figure 5. Sulfide-bearing rocks from the Lion Hill area. All scales in centimeters. *A*, Sphalerite and galena (s) in elongate metamorphic segregations along schistosity/shear surfaces parallel to bedding (core N24 at 158.8 m). *B*, Intergranular sphalerite, galena, and chalcopyrite (s) in matrix-supported dolostone breccia (core N14 at a depth of 166.7 m). *C*, Intergranular sphalerite (s, medium-gray material) in cross-stratified metasandstone (drillhole N28 at a depth of 158.5 m). *D*, Discordant fracture filled with material from surrounding rock including trace amounts of sphalerite (core L2 at a depth of 24 m). *E*, Discordant, massive sphalerite (s) vein cutting gray dolostone and vein of calcite-cemented solution breccia(?) (drillhole L2 at a depth of 82.3 m). *F*, Layered magnetite iron formation with later quartz veining. Darkest bands are sulfide and magnetite rich; lighter bands are silicate rich.

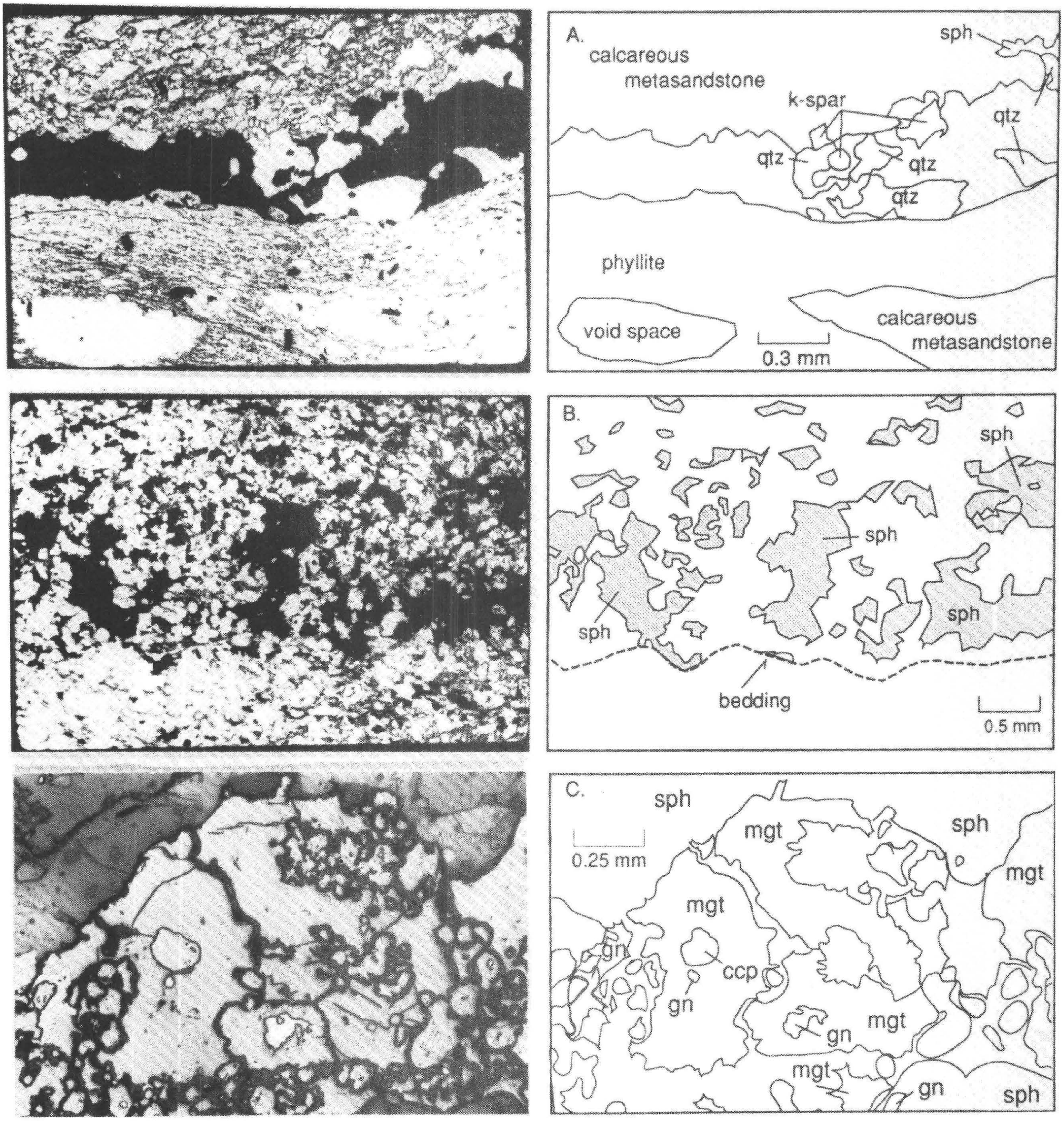
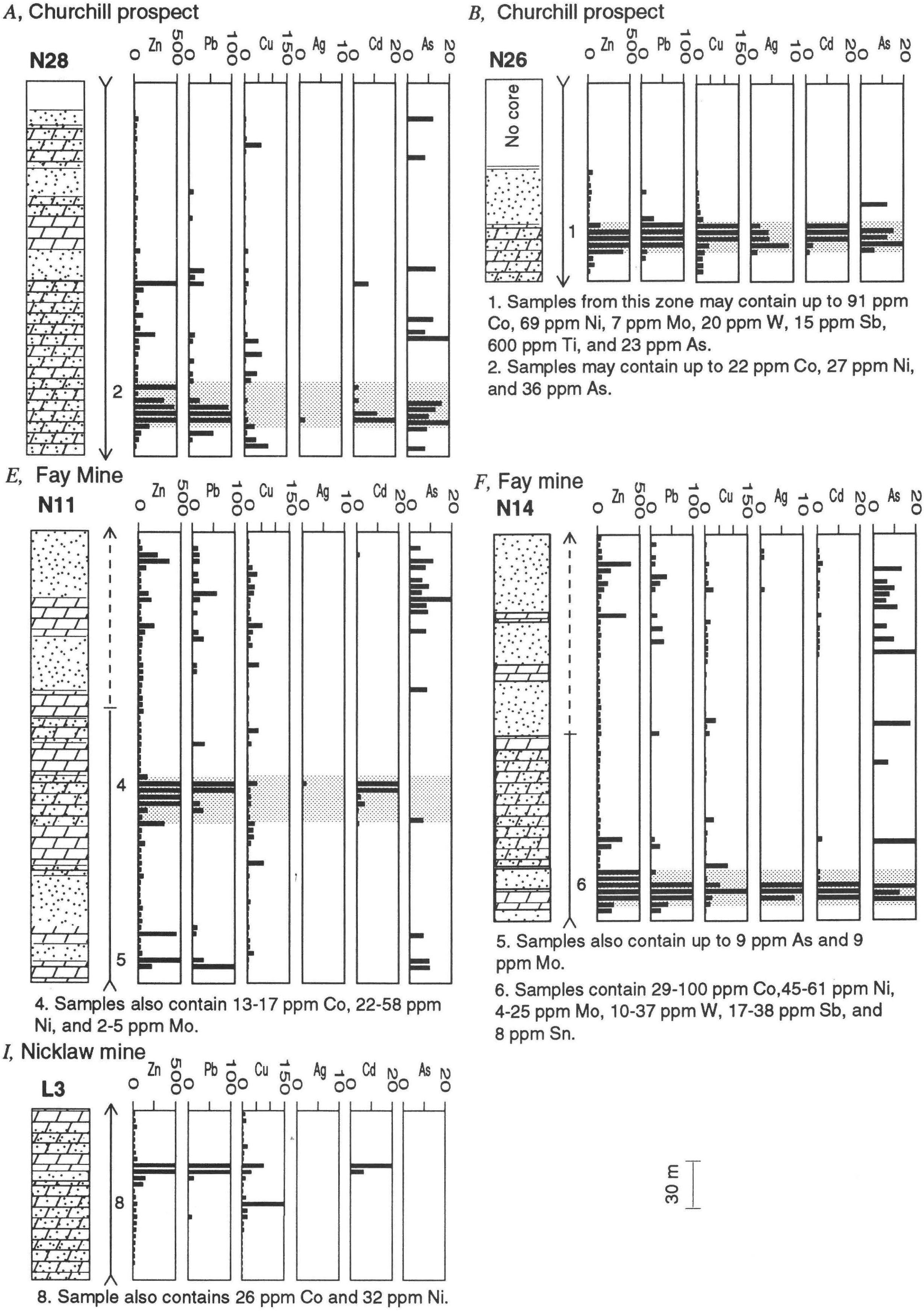


Figure 6. Photomicrographs of sulfide-rich samples from the Lion Hill area. Abbreviations: ccp, chalcopyrite; gn, galena; k-spar, K-feldspar; mgt, magnetite; qtz, quartz; sph, sphalerite. *A*, Sulfides (black) in metamorphic segregation parallel to schistosity, plane transmitted light (from core B24 at a depth of 16.2 m). *B*, Interstitial sphalerite (black) concentrated in slightly less calcareous bed of calcareous metasandstone, plane transmitted light (sample from core B31 at a depth of 227.1 m). *C*, Inclusions of galena in magnetite from iron formation, reflected light (sample from dump near Nicklaw mine).

Monkton Quartzite and Winooski Dolomite (figs. 3, 4*B*). Cores N10 and N13, which were drilled south and southeast of the Fay mine (figs. 3, 4*B*), contain a much greater proportion of carbonate than cores that intersect the mineralized zones. Core L3 (fig. 7*I*) intersects a weakly mineralized zone in Monkton Quartzite at the Nicklaw mine, north of the two main mineralized areas (fig. 3).

The patterns of metal distribution for the southern and northern ore lenses show that Zn, Pb, Cu, and Cd are the most strongly concentrated elements in the mineralized



1. Samples from this zone may contain up to 91 ppm Co, 69 ppm Ni, 7 ppm Mo, 20 ppm W, 15 ppm Sb, 600 ppm Ti, and 23 ppm As.

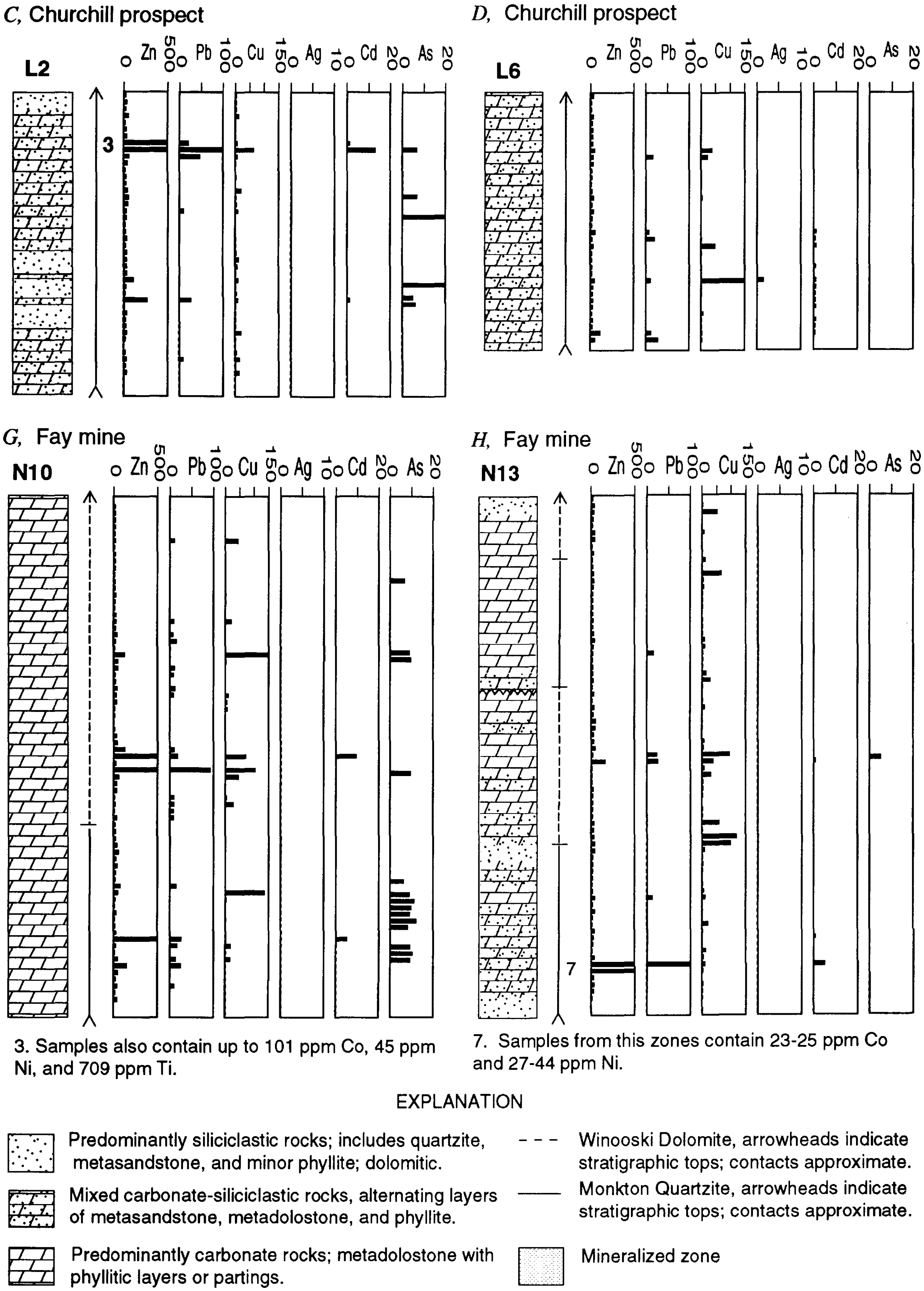
2. Samples may contain up to 22 ppm Co, 27 ppm Ni, and 36 ppm As.

4. Samples also contain 13-17 ppm Co, 22-58 ppm Ni, and 2-5 ppm Mo.

5. Samples also contain up to 9 ppm As and 9 ppm Mo.

6. Samples contain 29-100 ppm Co,45-61 ppm Ni, 4-25 ppm Mo, 10-37 ppm W, 17-38 ppm Sb, and 8 ppm Sn.

8. Sample also contains 26 ppm Co and 32 ppm Ni.



3. Samples also contain up to 101 ppm Co, 45 ppm Ni, and 709 ppm Ti.

7. Samples from this zones contain 23-25 ppm Co and 27-44 ppm Ni.

EXPLANATION

Predominantly siliciclastic rocks; includes quartzite, metasandstone, and minor phyllite; dolomitic.

Mixed carbonate-siliciclastic rocks, alternating layers of metasandstone, metadolostone, and phyllite.

Predominantly carbonate rocks; metadolostone with phyllitic layers or partings.

- - - Winooski Dolomite, arrowheads indicate stratigraphic tops; contacts approximate.

—— Monkton Quartzite, arrowheads indicate stratigraphic tops; contacts approximate.

Mineralized zone

Figure 7. Generalized lithologies and contents of Zn, Pb, Cu, Ag, Cd, As, and other elements (in parts per million) present in anomalous amounts (indicated by footnotes) in samples selected to show characteristic geochemical patterns from west to east in the Churchill prospect area (*A–D*), from west to east in the Fay mine area (*E–H*), and in the Nicklaw mine area (*I*). Shaded areas highlight established mineralized zones. Locations of drillholes are shown in figures 3 and 4. See text for analytical details.

zones (fig. 7*A*, *B*, *E*, *F*). Zinc has a high elemental abundance (up to >20,000 ppm) throughout the ore lenses, whereas Pb is generally most enriched (up to >19,000 ppm) in the central, higher grade parts of mineralized zones. The pattern of Cu enrichment (up to 14,000 ppm) is similar to that of Pb in mineralized zones. The correlation of Cd (up to 560 ppm) and Zn suggests that Cd occurs in sphalerite because no other Cd-bearing phase such as greenockite is present at Lion Hill. Arsenic is also enriched greatly in the mineralized zones in three of the four drillholes (up to 40 ppm). The distribution of Ag is erratic; Ag was found in anomalous amounts (up to 60 ppm) throughout some highly mineralized zones (for example, N26, N14), but was barely detected (<5 ppm) in others (N28, N11).

Patterns of elemental abundance for the Nicklaw mine area match those described above for the southern and northern mineralized zones (fig. 7*I*). Samples of drillcore indicate that Zn, Pb, Cu, and Cd are concentrated in the weakly mineralized ore zone. Silver was not detected. Three samples of the magnetite iron formation collected at the mine dump were analyzed (table 2 of Clark, 1990). All three iron formation samples show concentrations of Fe (>24 ppm), V (>1,000 ppm), Zn (>10,000 ppm), Pb (>1,000 ppm), and Cu (>1,500 ppm) that are well above the upper limit of determination. In addition, these samples have high concentrations of Ag (19–84 ppm), Cd (620–840 ppm), Ni (160–210 ppm), Co (23–31 ppm), and Se (8.1–24 ppm); Au was not found (below detection level of 0.08 ppm).

Zinc and Pb are generally the most widely distributed metals laterally in weakly mineralized halos surrounding the main mineralized zones; Cu and As show minor enrichment. For example, cores L2, L6, N10, and N13 all contain anomalous concentrations of either Zn, Pb, Cu, or As (fig. 7*C*, *D*, *G*, *H*). Copper, and to some extent As, are present in slightly anomalous amounts in samples that lack anomalies in other metals (for example, L2, L6, table 1).

RELATION TO STRATIGRAPHY

Reconstructing the stratigraphic section for the area (fig. 8) was accomplished by unfolding the structures, making contacts generally horizontal, and positioning the sections relative to (1) the Monkton-Winooski contact, (2) possibly correlative siliciclastic layers, and (3) zones containing high contents of base-metal elements. The reconstruction of the stratigraphy and mineralized horizons is heavily dependent on data for drillhole N11, near the Fay mine, because this section contains three metal-rich horizons, the Monkton-Winooski contact, and a variety of lithologies for rough correlation. The sections are positioned relative to the sedimentary contact and mineralized horizons. Individual lithologies are generally not perfectly correlatable, as described earlier. Figure 8 indicates that the complete vertical interval of mineralized rock may be on the order of 250 m, although mineralization was strongest in three broadly stratabound horizons within the interval that have thicknesses of about 30 to 100 m or less and are spaced approximately 50 and 100 m apart. The bulk of the highly mineralized rock is contained in the middle horizon, located about 50 m below the Monkton-Winooski contact (fig. 8). Weaker horizons above and below the middle horizon may be a halo effect or may represent separate mineralizing events.

The mineralized zones generally occur in mixed carbonate-siliciclastic rocks, at or above prominent well-sorted siliciclastic units (N26, N28, N11, and N14, at ~0 m, ~50 m ~30 m, and ~0 m above, respectively) (fig. 7*A*, *B*, *E*, *F*). Weak mineralization occurs in some well-sorted siliciclastic units (N11, N14) and in dominantly carbonate units (N10, N13).

FLUID-INCLUSION STUDY

Coarse crystals of sphalerite up to 5 mm in width were selected from four cores (total of 7 localities) intersecting the main mineralized lenses (N26, N14, N28, and L2). These crystals form discordant veins, some of which show evidence of open-space filling. Other occurrences of sphalerite (as intergranular aggregates and unambiguous metamorphic segregations) and most other minerals were too fine grained to contain inclusions suitable for analysis. The 20- to 50-µm-wide liquid-vapor inclusions fall into two groups based on textural characteristics. They do not contain daughter minerals, trapped solids, or visible CO_2. The majority of the inclusions are secondary in nature and are aligned along healed microfractures; others, having the same general size range, are isolated or occur in small groups and may be primary in origin.

FLUID-INCLUSION DATA

Fluid-inclusion thermometry results for sphalerite from discordant veins of the Lion Hill deposit (Foley, 1990) are plotted on figure 9. Homogenization temperatures of possible primary inclusions in sphalerite (table 2) range from 152° to 196°C. Measurements of the bulk salinity of the same inclusions, based on temperatures of the melting point of ice, yielded values of 11.5 to 14 equivalent wt% NaCl. Eutectic temperatures of about −25° to −30°C suggest that sodium is the dominant cation in solution. The lack of daughter minerals in the inclusions at room temperature indicates that the solutions are undersaturated with respect to the common salt components. Both primary and secondary groups of inclusions yielded approximately the same ranges of temperature and salinity values, implying that the two groups of inclusions contain cogenetic fluids. The inclusions lack textural evidence for having formed in a boiling environment.

Table 1. ICP–AES analyses of drillcore samples from mineralized, weakly mineralized, and unmineralized intervals from the northern mineralized area, the southern mineralized area, and the Nicklaw mine area and farther north (fig. 3).

[Results are given in ppm and are rounded to two significant figures. *, near detection limit; 0, not detected]

Core	Depth[1]	Width[2]	Zn	Pb	Cu	Ag	Cd	As	Co	Ni	Mo	Sb	W	Lithology[3]
Southern mineralized area														
N11	112.5	24.4	33–24,000	0–1,400	2.2–33	0	0–66	0–6.1	3.6–18	11–58	0–5.9	0	0	m- Dolostone.
N11	162.2	21.9	16–48	0	1.3–8.6	0	0	0	2.6–8.1	10–23	0	0	0	u- Quartzite.
N11	184.1	20.1	18–640	0–140	1.9–20	0	0	0–9.4	2.1–35	6.9–58	0–8.5	0	0	w- Dolostone and quartzite.
N14	154.8	15.8	24–>2,000	0–15,000	0–1,400	0–59	0–560	0–40	3.1–100	3.3–61	0–2.5	0–84	0–37	m- Dolostone.
N10	112.2	14.6	13–2,100	0–92	*0.7–103	0	0–9.3	0–*9.1	<6.0–27	0–36	<1.2	0	0	w- Dolostone.
N10	197.2	5.2	19–2,200	*9.1–25	0–16	0	0–4.9	0–*9.5	<6.0	*4.3–8	<1.2–*1.3	0	0	w- Dolostone.
N13	210.3	6.1	500–>2,400	0–190	3.8–9.5	0	0–5.0	0	23–25	27–44	0	0	0	w- Dolostone.
L4	68.0	6.4	16–85	0–140	1.3–30	0	0	0–31	4.1–11	4.0–11	0	0	0	w- Dolostone.
L4	112.2	5.2	110–170	0	1.5–2.7	0	0	0	4.1–4.5	2.5–3.1	0	0	0	w- Siliceous dolostone.
Northern mineralized area														
N26	64.3	14.6	8.2–21,000	0–7,800	2.3–250	0–8.7	0–190	0–23	3.0–91	5.2–69	0–7.4	0–15.1	0–21	m- Siliceous dolostone.
N28	144.2	20.4	42–>3,000	0–1,900	0–34	0–*1.2	0–82	0–36	<.6–22	0–27	0	0	9.6–19	m- Metasandstone.
L2	20.1	10.3	58–>2,400	15–100	4.6–63	0	0–13	0–6.6	5.8–26	4.6–32	0	0	0	w- Dolostone.
L2	81.7	11.9	18–270	0–26	1.5–8.3	0	0–1.2	0–26.0	2.8–14	3.4–18	0	0	0	w- Dolostone and quartzite.
L6	24.4	7.0	13–48	0–17	5.5–38	0–*1.4	0	0	3.0–8.3	7.6–110	0	0	0	w- Dolomitic metasandstone.
Nicklaw mine area and to the north														
L3	23.8	5.2	>22,000	140–820	7.1–76	0	6.1–34	0	5.6–7.3	8.3–8.9	0	0	0	w- Dolostone.
L5	0.7	90.8	12–50	0–8	0.3–34	0	0	0	2.8–7.5	2.8–18	0	0	0	u- Dolostone.

[1] Depth to the top of the analyzed interval in meters.

[2] Width of analyzed interval in meters.

[3] m, mineralized zone; we, weak mineralization or anomalous Zn, Cu, or Pb; u, unmineralized.

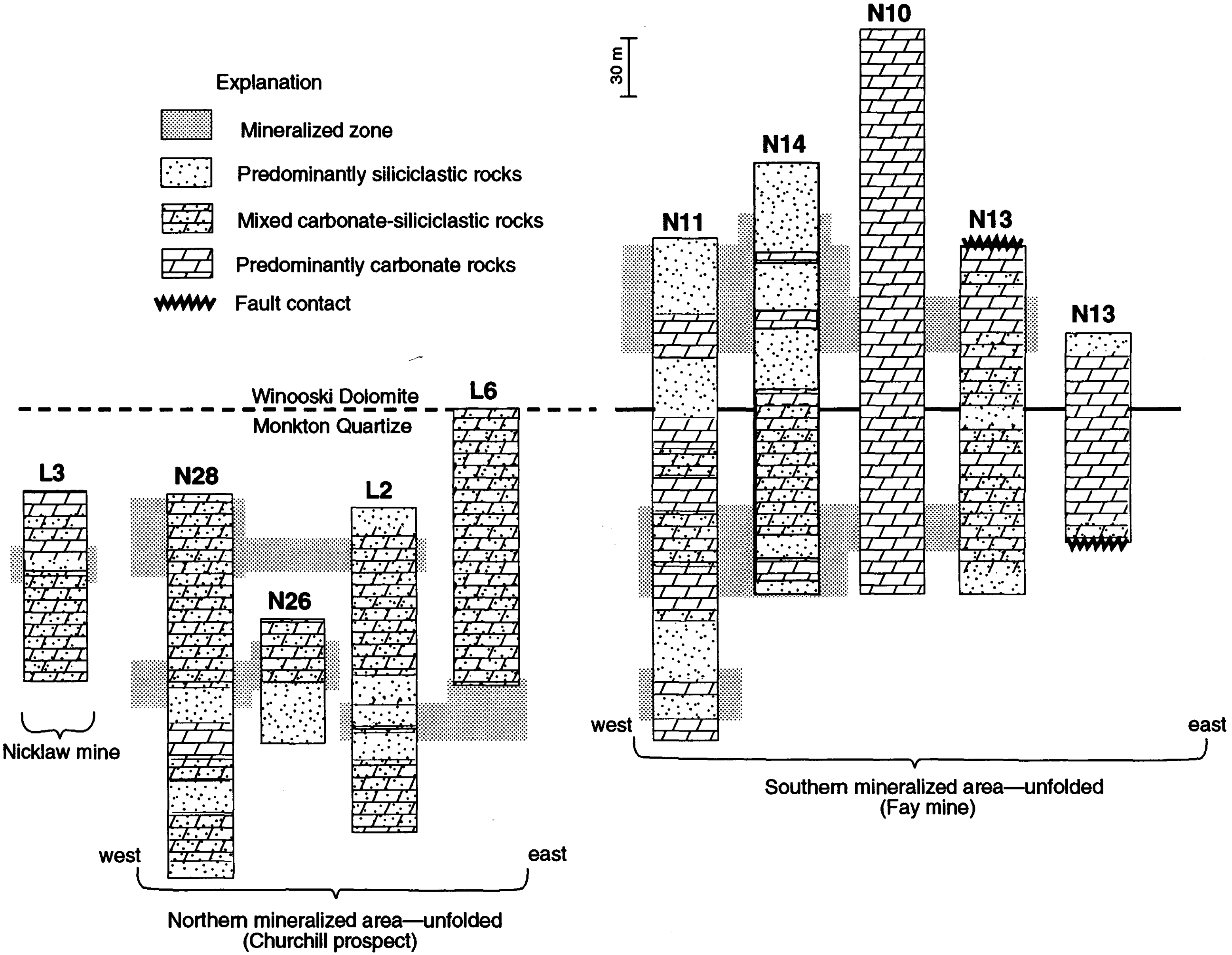


Figure 8. Reconstructed stratigraphic section for the Lion Hill area showing combined geochemical profiles.

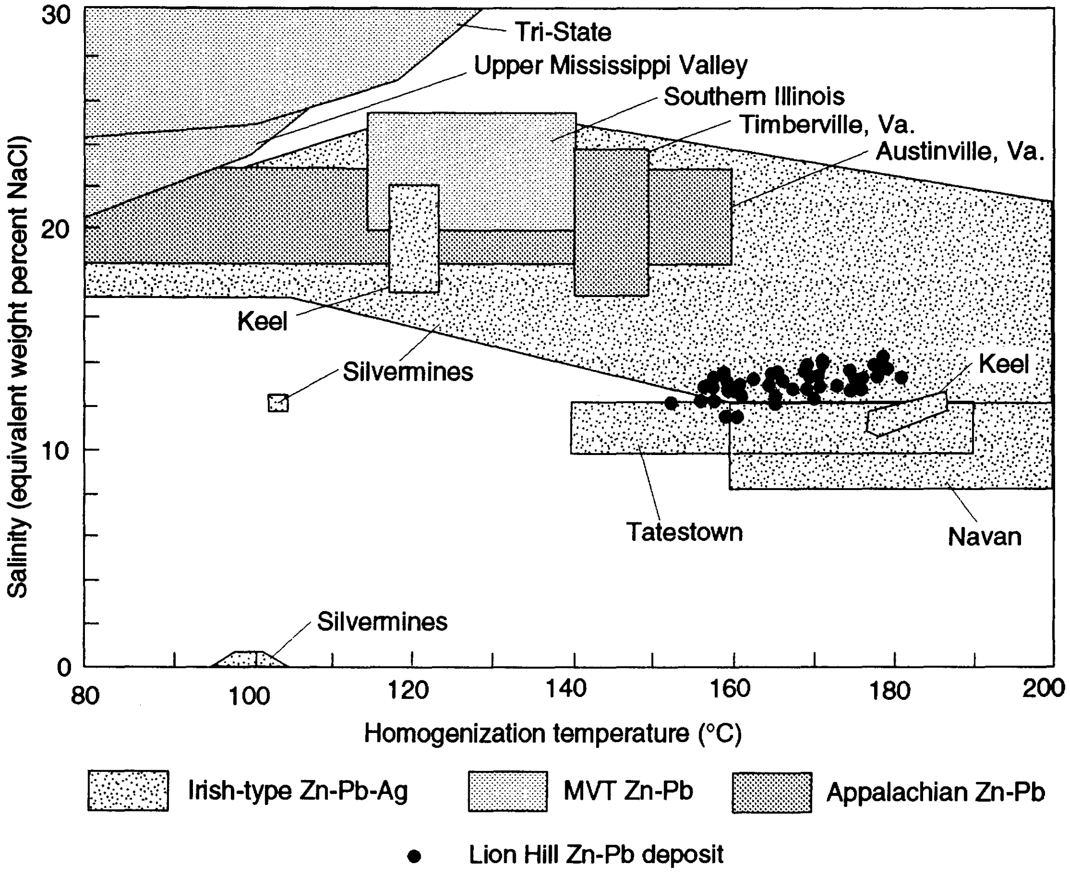


Figure 9. Temperature-salinity relations for fluid inclusions in sphalerite from discordant veins at Lion Hill (filled circles). For comparison, fluid-inclusion data are plotted for Mississippi Valley-type (MVT) deposits (Upper Mississippi Valley, Tri-State, and Southern Illinois districts, Roedder, 1976), Appalachian-type Zn-Pb districts (Austinville, Va., Foley and Craig, 1989; Timberville, Va., Roedder, 1976), and Irish carbonate-hosted deposits (Silvermines, Samson and Russell, 1984; Navan and Tatestown, Andrew and Ashton, 1985; Keel, Roedder, 1976, Caulfield and others, 1986).

DISCUSSION OF DATA

Discordant veins at Lion Hill may have originated either as epigenetic veins that were conduits or feeder zones for near-surface exhalations or as open-space fillings of sulfides remobilized along small fractures and shears related to regional metamorphism during the Taconic orogeny. Larger pods of sulfide minerals that occur as apparent segregations along shears and fractures, and in small discordant veinlets, have small halos of recrystallized dolomite indicating that the minerals may have recrystallized. These textures can be accounted for by reactions of hot saline, water-rich fluids with the carbonate wallrock in a feeder zone or by recrystallization during metamorphism. Thus, fluids trapped in the inclusions may represent either diagenetic fluids related a feeder zone or fluids that were present during and after the peak metamorphic event.

MODEL FOR A DIAGENETIC ORIGIN

Mineralizing fluids that precipitated synsedimentary and diagenetic sulfides near the seawater-sediment interface must have originated at depth and traveled through faults, fractures, and structurally weak zones in the sedimentary pile. Under the simple hydrostatic conditions expected to prevail in this environment (fluid column open to air-water interface), the thermometry data can be used to infer that the discordant veins formed at depths ranging from 30 to 135 m (based on data of Haas, 1971) below the air-water interface. Elevated salinities are typical of many basinal brines and may indicate that the fluids interacted with an unknown evaporite sequence at depth; however, ultrafiltration and boiling to generate higher salinities also are possible explanations. Evaporitic conditions have been proposed to be an integral part of the supra-, inter-, and shallow subtidal environments indicated for the Lion Hill sedimentary

Table 2. Fluid-inclusion homogenization temperature and salinity data for sphalerite from Lion Hill, Vt.

Inclusion No.	Th (°C)	Tm (°C)	Salinity[1] (wt % NaCl)
1	168		
2	177		
3	150.9		
4	160.1	−7.8	11.47
5	159.3	−7.8	11.47
6	164.2		
7	165.1	−8.4	12.19
8	170.1	−8.4	12.19
9	159.3		
10	152.4	−8.3	12.07
11	169.2	−8.9	12.76
12	175	−8.9	12.76
13	176	−9	12.88
14	172.7	−8.9	12.76
15	156		
16	165	−8.7	12.53
17	167.6	−8.9	12.76
18	159.1	−8.8	12.65
19	156.2	−8.5	12.3
20	176	−9.3	13.22
21	170.4	−9.2	13.1
22	166.5		
23	171.2	−9.2	13.1
24	170.3	−9.2	13.1
25	169.4	−9.1	12.99
26	177.8	−9.8	13.77
27	178.6	−10	13.99
28	178.7	−9.8	13.77
29	178.3	−9.8	13.77
30	157.4	−8.5	12.3
31	164.8	−9	12.88
32	162.5	−9.2	13.1
33	160.4	−8.8	12.65
34	161.8		
35	165.3	−9.4	13.33
36	169	−9.5	13.44
37	169.1	−9.4	13.33
38		−9.4	
39	156.7	−9	12.88
40	157.8	−9.2	13.1
41	160.8	−9	12.88
42	157.4	−9	12.88
43	158.1		
44	159	−9.1	12.99
45	169.1	−9.7	13.66
46	166	−9.3	13.22
49	165	−9.5	13.44
50	168.9	−9.6	13.55
51	158.9	−9.5	13.44
52	175.8	−9.3	13.22
53	198	−9.5	13.44
54	174.7	−9.6	13.55
55	161.2	−8.6	12.42
56	165.3	−8.7	12.53
57	171	−9.9	13.88
58	171.2	−9.8	13.77
59	181	−9.2	13.1
60	178	−9.2	13.1

[1] Total salinity expressed in equivalent weight percent NaCl using data of Hall and others (1988).

sequence (Clark, 1990; Mehrtens, 1985), although mineralogical evidence for evaporites is no longer present in the rocks, perhaps due to regional metamorphism related to the Taconic orogeny. The hot, saline solutions would provide a ready transport mechanism for the metals as chloride complexes. Possible precipitation mechanisms operating both in the epigenetic veins and at the seawater-sediment interface include mixing with a less saline, cooler fluid (for example, seawater), cooling by conduction, or a combination of these.

This model for the inclusion data assumes that the inclusions in sphalerite withstood metamorphic overprint of the Taconic orogeny. Because such a scenario is unlikely without some degree of remobilization and reprecipitation, and due to the uniformity of data for secondary and primary inclusions, a metamorphic model is also presented.

MODEL FOR A METAMORPHIC ORIGIN

If the discordant veins formed as a result of a regional metamorphic overprint, as originally interpreted by Foley (1990), they would probably contain minerals that formed by remobilization and recrystallization of preexisting sulfide enrichments. The original inclusion fluids may not have survived the deformation and recrystallization of the Taconic orogeny, and additional metamorphic fluids probably were generated by dewatering of the enclosing sedimentary rocks. The fluid preserved in inclusions in minerals that form in this manner may represent a combination of intercrystalline fluid, derived by the release of fluids trapped within inclusions in precursor sulfides and gangue minerals, and interstitial pore fluids. The fluid compositions obtained for Lion Hill are consistent with local metamorphosed rock and mineral assemblages. The lack of visible CO_2 in the fluid inclusions is consistent with the low regional metamorphic grade and suggests that little or no additional fluid was generated *in situ* by decarbonation reactions. Additional fluids possibly were added by migration of ground water to the site during metamorphism.

Homogenization temperatures for the inclusions are somewhat cooler (~100–200°C) than probable peak metamorphic temperatures in the study area (Foley, 1990). During Middle Ordovician time, prior to Taconic thrusting and deformation, at least 1,000 m of sedimentary rock overlay the Monkton Quartzite in the vicinity of Lion Hill (Cady, 1945). Medium-pressure regional metamorphic environments generate lithostatic pressures of about 2–4 kbar at temperatures of around 400°C. Thus, the minerals could have formed at pressures as great as 4 kbar. Corrections to homogenization temperatures due to lithostatic pressure developed under peak metamorphic conditions are impossible to estimate accurately; however, they may be on the order of 200°C or less (Hall and others, 1988). A more likely scenario may be that the sphalerite formed during a retrograde stage of metamorphism when the fluids cooled along with a decrease in the regional temperature and pressure.

ISOTOPE STUDIES

SULFUR ISOTOPIC DATA

Several small sulfide deposits hosted by the Dunham Dolomite and Monkton Quartzite were previously analyzed for sulfur isotopes by Boucher (1986). Three galena and four sphalerite samples from mineralized zones near Dunham, Quebec, and Franklin, Vt., have $\delta^{34}S$ values from –9.5 to +0.8‰, and separates of sphalerite and galena from the Brandon prospect at Lion Hill had $\delta^{34}S$ values of –9.3‰ and –11.3‰, respectively. These values are similar to results of sulfur isotopic analyses from Lion Hill in this study (table 3, fig. 10). The entire range of values for galena, chalcopyrite, sphalerite, and pyrite is from –25.9‰ to +10.0‰, with marked distinctions among the different minerals. Galena, sphalerite, and chalcopyrite (–17 to +3‰) generally are isotopically lighter than pyrite that occurs as cubes disseminated in the sedimentary rocks (0 to +10‰). Pyrite from sample L6–162 which occurs as an intergrowth with other sulfides (lowermost mineralized zone, fig. 8) has a value of –25.9‰. Three sphalerite samples with $\delta^{34}S$ values near +2.5‰ occur as irregular discordant veins (lowermost mineralized zone). The only apparent cogenetic pair of galena and sphalerite measured (N12–526), gave a temperature of about 500°C, which suggests disequilibrium sulfur isotopic fractionation between the two sulfides if they formed from syngenetic or diagenetic processes.

Metamorphism and deformation of the Lion Hill deposit may have remobilized sulfides, but their effect on the sulfur isotopic composition of sulfides should be minimal, resulting in only a slight homogenization of values (Schwarz and Burnie, 1973). Thus, the wide variation in sulfur isotopic values of the sulfides from Lion Hill probably reflects sulfur isotopic variations present in the original depositional environment.

A sulfide separate from magnetite iron formation at the Nicklaw mine has a $\delta^{34}S$ value of –14.3‰. Galena from the Fernville deposit in the Dunham Dolomite has a $\delta^{34}S$ value of –6.0‰, and galena from the White Creek deposit has a value of –14.9‰.

Discussion.—The major source of sulfur for most sediment-hosted base metal deposits is interpreted to be contemporaneous seawater sulfate (Coomer and Robinson, 1976; Boast and others, 1981; Caulfield and others, 1986, Sangster, 1990). The relatively narrow range of sulfur isotopic values for barite in these deposits that is similar to values for contemporaneous seawater sulfate is evidence for a seawater sulfate source. Additional evidence is that sulfur isotopic values for sulfide minerals are about 25 to 50‰ lighter than coexisting sulfate, which is the expected kinetic fractionation for bacterial reduction of sulfate under different environmental conditions (Schwarz and Burnie, 1973; Ohmoto and Rye, 1979). The lack of barite at the Lion Hill deposit makes it difficult to fully constrain the source of sulfur, but contemporaneous seawater sulfate is the most probable source of the bulk of the sulfur in the Lion Hill deposit. Early Cambrian seawater had probable $\delta^{34}S$ values ranging from 25 to 30‰ (Claypool and others, 1980). The range of $\delta^{34}S$ values for sulfides from Lion Hill, from –25.9 to +10.0‰, falls within the expected range for sulfide produced by bacteriogenic reduction of Early Cambrian seawater sulfate.

Kinetic fractionation between sulfate and sulfide during bacterial reduction is dependent on the rate of reduction, which in turn is dependent on the type and supply of nutrients for sulfate-reducing bacteria (Ohmoto and Rye, 1979). An open system, such as a euxinic basin, has a constant supply of sulfate, and the kinetic fractionation factor between sulfate and sulfide will remain nearly constant, with values between 40 and 60‰ (Schwarz and Burnie, 1973). Closed systems, such as shallow-marine or brackish tidal basins, have limited supplies of nutrients, and the rate of sulfide production outstrips the sulfate supply with the result that the kinetic fractionation factor is near 25‰ (Schwarz and Burnie, 1973). Closed-system behavior also may be a factor when seawater is trapped as pore fluid in wet sediments and shut off from a supply of nutrients in overlying seawater (Schwarz and Burnie, 1973; Sweeney and Kaplan, 1980). The majority of $\delta^{34}S$ values for galena and sphalerite from the middle mineralized zone of the Lion Hill deposit (fig. 8) fall between –6.6 and –16.8‰, approximately 35 to 47‰ lower than Early Cambrian seawater sulfate, consistent with bacterial reduction of sulfate in an open system. The single pyrite value of –25.9‰, from pyrite associated with galena and sphalerite in the lowermost mineralized zone (fig. 8), also is typical of pyrite formed by the reduction of seawater sulfate in an open system. However, pyrite and sphalerite $\delta^{34}S$ values greater than 0‰ are more consistent with closed-system behavior or may indicate a source of sulfur other than contemporaneous seawater sul-

Table 3. Sulfur isotopic data for the Lion Hill deposit, Vt., and the Fernville, Vt., and White Creek, N.Y., prospects.

Sample No.	δ^{34}S (‰)	Mineral[1]	Host[2]	Lithology[3]	Texture[4]
			Lion Hill, Vermont—southern mineralized mine		
L1-120	+.1	Py	MQ	Dol	E: Fine-grained pyrite along fractures.
L1-124	−6.6	Sph	MQ	Dol	B
L4-268	+7.7	Py	MQ	Dol	E: Pretectonic cubes (early).
N16-283	+6.2	Py	WD	Ph	D: In late quartz vein that cuts earlier mineralization.
N14-547	−11.4	Sph	MQ	Dol	C
N12-526	−16.8	Gn	MQ	Dol	A: Matrix of dolomite.
N12-526	−15.7	Sph	MQ	Dol	? : Breccia.
N10-338	+5.8	Py	WD	Dol	E: Fine cubes along small fractures.
N10-387	+5.8	Py	WD	Dol	E: Coarse to fine cubes, pretectonic.
N15-65	−10.0	Py	WD	Ph	E: Fine to coarse cubes, disseminated.
N17-692	−14.2	Gn	MQ	Dol	D: Calcite crystals along fractures in dolomite with galena.
			Lion Hill, Vermont—northern mineralized zone		
N24-53	−13.3	Gn	MQ	Ss	A: Breccia matrix.
N24-64	+2.5	Sph	MQ	Dol	D: Late dolomite vein, green sphalerite, open space filling.
N26-240	−15.3	Gn	MQ	Dol	C
N27-2835	−8.3	Sph	MQ	Dol	D: Crystals in cross-cutting dolomite veins.
N27-423	−13.9	Sph	MQ	Dol	A: Breccia in matrix.
N28-520	−14.8	Sph	MQ	Dol	B
N28-525.5	−15.7	Sph	MQ	Ss	A: Intergranular in cross-bedded sandstone.
N28-526	−11.7	Sph	MQ	Dol	B
N31-50	−13.7	Gn	MQ	Dol	D: Crystals in coarse dolomite veins.
L2-36	−3.0	Cpy	MQ	Ph	B
L2-84	−10.6	Sph	MQ	Dol	B
L2-270-1	+2.1	Sph	MQ		C: Late sphalerite, cuts dolomite vein.
L2-270-2	+2.5	Sph	MQ		C: Late sphalerite, cuts dolomite vein.
L2-364	+4.6	Py	MQ	Ph, Dol, Ss	E: Fine-grained aggregated pressure features, pretectonic.
L6-92	+4.9	Py	MQ	Ss	B: In fine fractures that cut bedding.
L6-162	−25.9	Py	MQ	Dol	D: Crystals in quartz-dolomite vein.
			Lion Hill—Nicklaw mine area		
L3-845	−12.2	Gn	MQ	Dol	B
L3-885	−10.6	Sph	MQ	Dol	B
VCs135A	−14.3	Sph	MQ	iron formation	A: Layered, with minor intergrown sulfides.
VCS135B	−11.5	Cpy	MQ	iron formation	A: Layered, with minor intergrown sulfides.
			Fernville, Vermont		
VCs301	−6.0	Gn	DD	Dol	Large galena crystal in quartz vein.
			White Creek, New York		
JS-86-5.1	−14.9	Gn	MPQ?		Crystal in galena-sphalerite matrix to quartzite.
JS-86-5.2	−14.7	Gn	MPQ?		Crystal in galena-sphalerite matrix to quartzite.

[1] Gn, galena; Sph, sphalerite; Cpy, chalcopyrite; Py, pyrite.

[2] DD, Dunham Dolomite; MQ, Monkton Quartzite; WD, Winooski Dolomite; MPQ, Mudd Pond Quartzite Member of the Nassau Formation.

[3] Dol, metadolostone; Ph, phyllite; Ss, metasandstone.

[4] A, intergranular; B, metamorphic segregation, along shears or small fractures; C, discordant veins; D, discordant veins with evidence of open-space filling; E, fine to coarse euhedral pyrite cubes, pretectonic.

fate. For example, pyrite occurs in some mineralized zones, as noted above for sample L6–162, but more commonly occurs as single cubes that are widespread in unmineralized host rocks. This form of pyrite, found in the uppermost, middle, and lowermost zones (fig. 8), probably formed by reaction between metal-bearing fluid and sulfate in trapped pore fluid, and this reaction resulted in more closed-system behavior and subsequently heavier sulfur isotopic values. The three sphalerite samples with δ^{34}S values between 2.0 and 2.5‰ occur in cross-cutting veins that are obviously

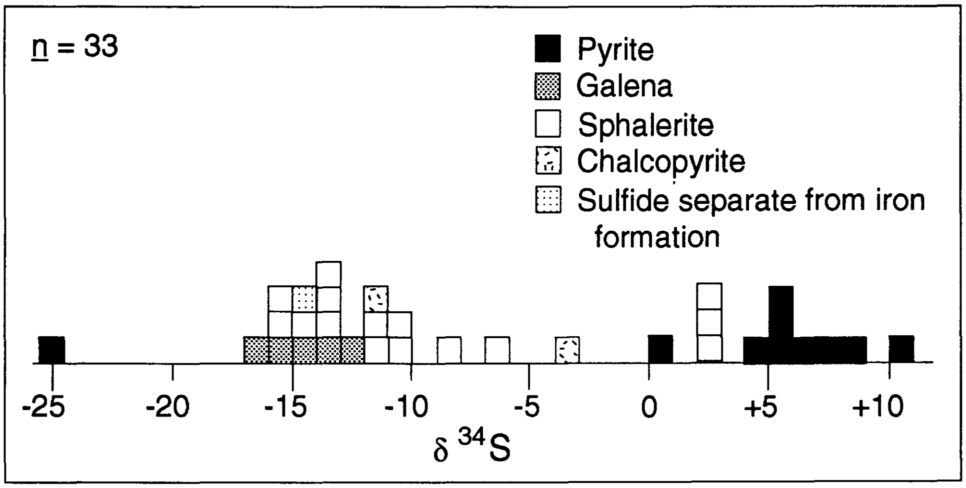


Figure 10. Sulfur isotopic compositions of sulfides from the Lion Hill deposit, including the magnetite iron formation.

later stage than the main stage of base-metal mineralization (see fig. 5*C*). The heavier sulfur isotopic values for these vein sphalerites may reflect a change in the source of sulfur, perhaps to deep-seated sulfur, during this later episode of mineralization. Several Irish sediment-hosted deposits with clusters of sulfur isotopic data ≥ 0‰ (Keel, Tatestown, and vein sulfides from Silvermines) are interpreted to have an additional minor, deep-seated source of sulfur near 0‰ (Coomer and Robinson, 1976; Caulfield and others, 1986).

LEAD ISOTOPIC DATA

Lead isotopic compositions of 12 galenas from mineralized localities are listed in table 4, together with sample numbers and host lithology. The analyses include data for nine samples from mineralized zones delineated by drillcore at Lion Hill and for one sample of magnetite iron formation from the Nicklaw mine dump (Foley, 1990). New data are presented for galena from the Fernville, Vt., Pb-Zn deposit (fig. 3), and for galena from the White Creek, N.Y., Pb-Zn deposit (fig. 1).

Lead isotopic compositions of the analyzed galenas are plotted on conventional lead isotopic diagrams in figure 11. Isotopic compositions of galenas from mineralized zones at Lion Hill range from 18.351 to 18.632 for ^{206}Pb/^{204}Pb, from 15.546 to 15.618 for ^{207}Pb/^{204}Pb, and from 38.126 to 38.496 for ^{208}Pb/^{204}Pb (table 4). Lion Hill galenas are moderately homogeneous, showing only a small spread in ^{206}/Pb/^{204}Pb (<5 times the measured standard deviation), in ^{207}Pb/^{204}Pb (<3 times), and in ^{208}Pb/^{204}Pb (<5 times). Galena from the magnetite iron formation, collected at the Nicklaw mine dump, is among the least radiogenic of galenas analyzed for the Lion Hill area (table 4).

Galena from the small mine at Fernville, Vt., has lead isotopic values that overlap the composition of galena contained within the Winooski Dolomite at Lion Hill. Sulfide minerals at Fernville are hosted by the Dunham Dolomite.

Lead isotopic values for galena from the White Creek mine (18.424 for ^{206}Pb/^{204}Pb, 15.563 for ^{207}Pb/^{204}Pb, and 38.264 for ^{208}Pb/^{204}Pb) are virtually identical to those for Lion Hill galenas. The small stratabound Pb-Zn deposit at White Creek, N.Y. (Slack and others, 1987; Clark and Slack, 1988) is in Lower Cambrian clastic rocks of a Taconic slope-rise sequence that ranges in age from Late Proterozoic to Middle Ordovician (Zen, 1967; Potter, 1972).

The lead isotopic values of galenas from the Lion Hill mineralized zones and iron formation, from the Fernville mine, and from the White Creek mine all yield model Pb-Pb ages based on the two-stage evolution curve of Stacey and Kramers (1975) of less than 212 Ma. The model ages are all significantly younger than the Early Cambrian age (approximately 550 Ma) of the host rocks and are much younger than mineralization or recrystallization of sulfides that may have taken place at 460–440 Ma, after the thermal peak of the Taconic orogeny (Zen, 1972, Sutter and others, 1985). Calculated ^{207}Pb/^{206}Pb isochron ages for the galenas yield geologically unreasonable estimates for the age of the source of the lead. Known basement rocks in the region are Proterozoic in age, and the deposits lie immediately to the west of ~1 Ga basement rocks that comprise the Green Mountain massif (fig. 1).

Discussion.—Compared to the growth curves of the plumbotectonic model of Doe and Zartman (1979) and the reference curve of Stacey and Kramers (1975), lead isotopic data for the Lion Hill galenas overlap the orogene curve and define a field that extends toward the mantle curve on a conventional ^{207}Pb/^{204}Pb-^{206}Pb/^{204}Pb diagram (fig. 12). The ranges in lead isotopic composition defined by these samples indicate that the lead was derived from a source or sources characterized by a somewhat variable lead isotopic composition. Because the data cannot be used to constrain

Table 4. Lead isotopic compositions of galenas from base-metal sulfide deposits hosted by carbonate-siliciclastic platform rocks of Vermont and the Taconic allochthon of New York.

Sample	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$	Lithology of wallrock[1]
Lion Hill deposit, Brandon, Vt.				
B-31-50'	18.351	15.546	38.275	Monkton Quartzite.
B-31-350'	18.463	15.552	38.368	Monkton Quartzite.
B-26-240'	18.496	15.592	38.406	Monkton Quartzite.
B-25-87'	18.483	15.587	38.404	Monkton Quartzite.
B-17-692'	18.378	15.551	38.126	Monkton Quartzite.
L3-84.5'	18.362	15.607	38.403	Winooski Dolomite.
L3-84'	18.442	15.583	38.465	Monkton Quartzite.
B-12-526'	18.374	15.566	38.318	Monkton Quartzite.
B-28-531'	18.632	15.618	38.496	Monkton Quartzite.
Magnetite iron formation, Nicklaw mine dump, Brandon, Vt.				
MIF-dump	18.253	15.536	38.496	Monkton Quartzite.
Fernville mine, Fernville, Vt.				
86VCS301	18.400	15.596	38.387	Dunham Dolomite.
White Creek mine, White Creek, N.Y.				
WC-1	18.424	15.563	38.264	Mudd Pond Quartzite Member of the Nassau Formation.

[1] See text for detailed geologic description of wallrock lithologies.

either the age of the mineralization or the age of the source, it is unlikely that age was the most important control on the lead isotopic composition of these occurrences.

A more likely factor controlling the isotopic composition of the galenas is the composition of different lead sources. Basement composition has been demonstrated to be the dominant control on the lead isotopic composition of galenas in carbonate-hosted base-metal deposits in western Newfoundland (Swinden and others, 1988). Carbonate-hosted Pb-Zn occurrences at Franklin, Vt., (fig. 11) are thought to have developed their distinctive lead isotopic signature by leaching of lead from the underlying Cheshire Quartzite via a sandstone aquifer model similar to that proposed by Doe and Delevaux (1972) for Mississippi Valley-type (MVT) deposits of southeast Missouri (Balogh, 1991). Schrijver and others (1988) have shown that $^{206}Pb/^{204}Pb$ values of galena in epigenetic veins increase from southwest to northeast in the northern Appalachians of Quebec, Canada. They attribute the variations in lead isotopic composition of the galenas to a progressive change in the type of detritus derived from Grenville basement during Cambrian and Ordovician time, from a less radiogenic lead component in the southeast that was derived from K-feldspar to a more radiogenic composition in the northeast that was derived from phyllitic material.

The lead isotopic composition of galena in the Lion Hill mineralization probably includes contributions from the sedimentary host rocks, their terrigenous sources, and lithologies traversed by the hydrothermal fluids that deposited the sulfide minerals. Although the isotopic composition of each of these sources may be distinct because of differences in the U/Pb and Th/U values of the rocks, the bulk lead isotopic composition measured in the galenas may reflect a regional lead fingerprint controlled by the integrated composition of basement source rocks in the area. Ayuso (1986) and Ayuso and Bevier (1991), in studies of basement terranes of Vermont, New Hampshire, and Maine in which they used plutonic rocks as geochemical probes of source regions, have identified important differences in the time-integrated lead isotopic compositions of Grenville and Avalonian basement terranes. A similar approach was tried for volcanogenic massive sulfide deposits in the Eastern United States and Canada (Slack and others, 1991). In figure 12, a field is shown outlining the data of Ayuso and Bevier (1991) for 400-Ma granitic plutons that have a source predominantly composed of Grenville basement as defined by rocks of the Adirondack, Green Mountain, and Chain Lakes massifs. The field for Lion Hill overlaps that of the Grenville source established by Ayuso and Bevier (1991) in $^{206}Pb/^{204}Pb$ and $^{207}Pb/^{204}Pb$, but has slightly higher values of $^{208}Pb/^{204}Pb$.

Possible local lead sources for the Lion Hill and Fernville deposits are the Cambrian and Ordovician carbonate-siliciclastic platform rocks, including the Dunham and Winooski Dolomites and Cheshire and Monkton Quartzites. Late Proterozoic to Middle Ordovician slates and graywackes of the Taconic allochthon, especially the Late Proterozoic and Lower Cambrian Nassau Formation, are possible local sources of the White Creek ores. Much of the lead in the terrigenous component of the Monkton Quartzite was probably derived originally from relatively unradiogenic feldspathic and more radiogenic phyllitic rocks of the

Proterozoic Grenville basement in the Adirondack Mountains (fig. 12; Zartman and Wasserburg, 1969). Selective weathering and erosion of coarser feldspathic versus finer grained phyllitic components would result in a mechanical separation of U/Pb reservoirs in the sedimentary sequence. Differential chemical leaching of lead and uranium by hydrothermal fluids could have further modified these reservoirs, resulting in dispersion in $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, and $^{208}Pb/^{204}Pb$ values.

COMPARISON WITH OTHER SEDIMENT-HOSTED BASE-METAL DEPOSITS

Fluid inclusions in sphalerite of the Lion Hill deposit have ranges of salinity and homogenization temperature that overlap those found for other occurrences of base-metal sulfides in rocks of the carbonate-siliciclastic platform in western Vermont. Fluid-inclusion measurements in sulfide samples from Dunham, Quebec, show a distribution of temperatures between 80° and 150°C and salinities of about 6 to 12 wt% NaCl equivalent (Boucher, 1986). Mineralized and unmineralized samples from Franklin, Vt. (~5 km south of Dunham, Quebec) yielded homogenization temperatures of fluid inclusions (Balogh, 1991) in sphalerite of 60–170°C and salinities of 8–12 wt% NaCl equivalent. Inclusions in quartz homogenized at 210–330°C and had salinities of 2–15 wt% NaCl.

The temperature ranges for fluid inclusions in sulfide minerals of the western Vermont platform rocks overlap those of MVT and Appalachian-type deposits, although the salinity range is considerably lower than that typical of MVT deposits (fig. 9). Primary inclusions from MVT deposits generally homogenize at temperatures that range from about 100° to 150°C (Roedder, 1976) for the main ore-forming stages (fig. 9). Inclusion data for the Austinville, Va., Appalachian-type deposit show a 100° to 160°C temperature range (Foley and Craig, 1989). The salinities of ore fluids in MVT and Appalachian-type deposits typically are much greater than 15 equivalent wt% NaCl, and commonly exceed 20 wt% NaCl equivalent (Roedder, 1976). Daughter crystals of halite are rarely found in these deposits; their scarcity suggests that there are appreciable quantities of ions other than sodium in the ore fluids.

The base-metal sulfide occurrences at Lion Hill and in other parts of western Vermont and southeastern Quebec have homogenization temperatures and salinities that match those of many of the Irish carbonate-hosted deposits (fig. 9), although the Lion Hill temperatures and salinities show more restricted ranges. Samson and Russell (1984) found that fluid inclusions in ore and gangue minerals from the Silvermines deposit homogenized at temperatures ranging from 50° to 260°C and had salinities primarily from about 0 to 24 wt% NaCl equivalent (fig. 9). Andrew and Ashton (1985) cite values of 8 to 12 equivalent wt% NaCl and 140° to 200°C for the Navan and Tatestown deposits of Ireland that also have been proposed to have formed in a synsedimentary-diagenetic environment (Andrew, 1986).

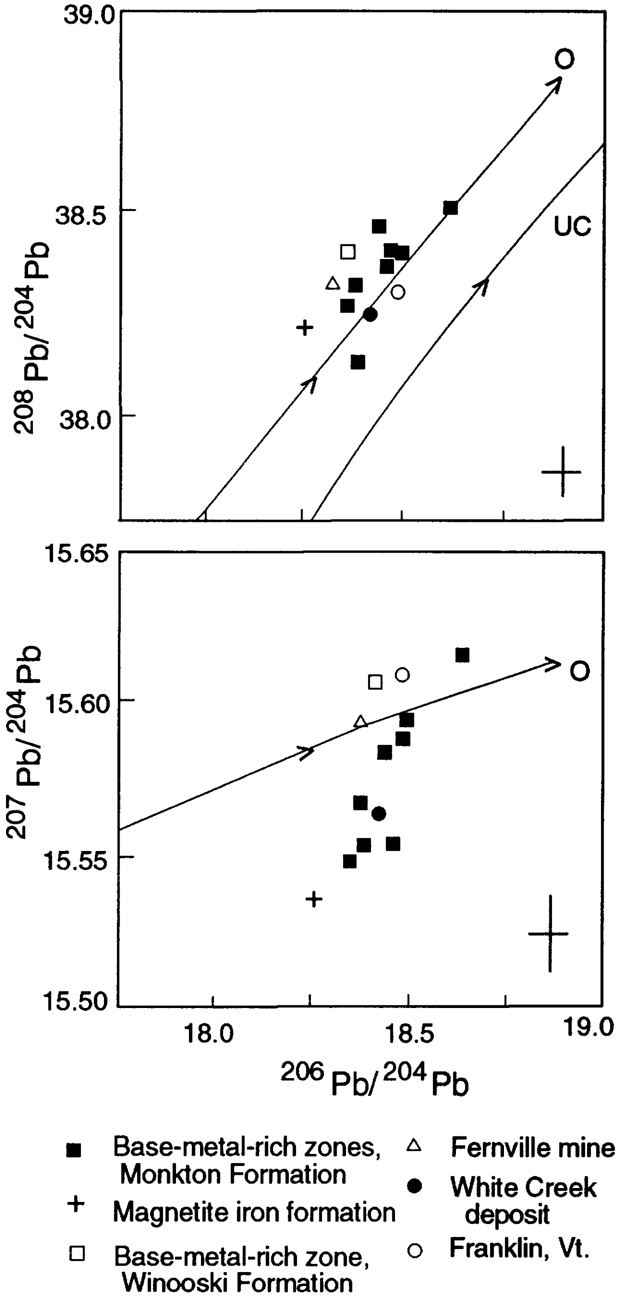


Figure 11. Lead isotopic data for galena from Lion Hill sulfide zones and magnetite iron formation near Brandon, Vt. Also shown are data points for a carbonate-hosted Pb-Zn deposit at Fernville, Vt., siliciclastic, sediment-hosted, stratiform Pb-Zn minerals at White Creek, N.Y., and an average galena composition for Zn-Pb minerals at Franklin, Vt. (Balogh, 1991). Orogene (O) and upper crust (UC) average lead evolution curves of Doe and Zartman (1979) are shown for comparison.

If the inclusions in sphalerite in the discordant veins at Lion Hill formed from trapped fluids in a feeder zone below

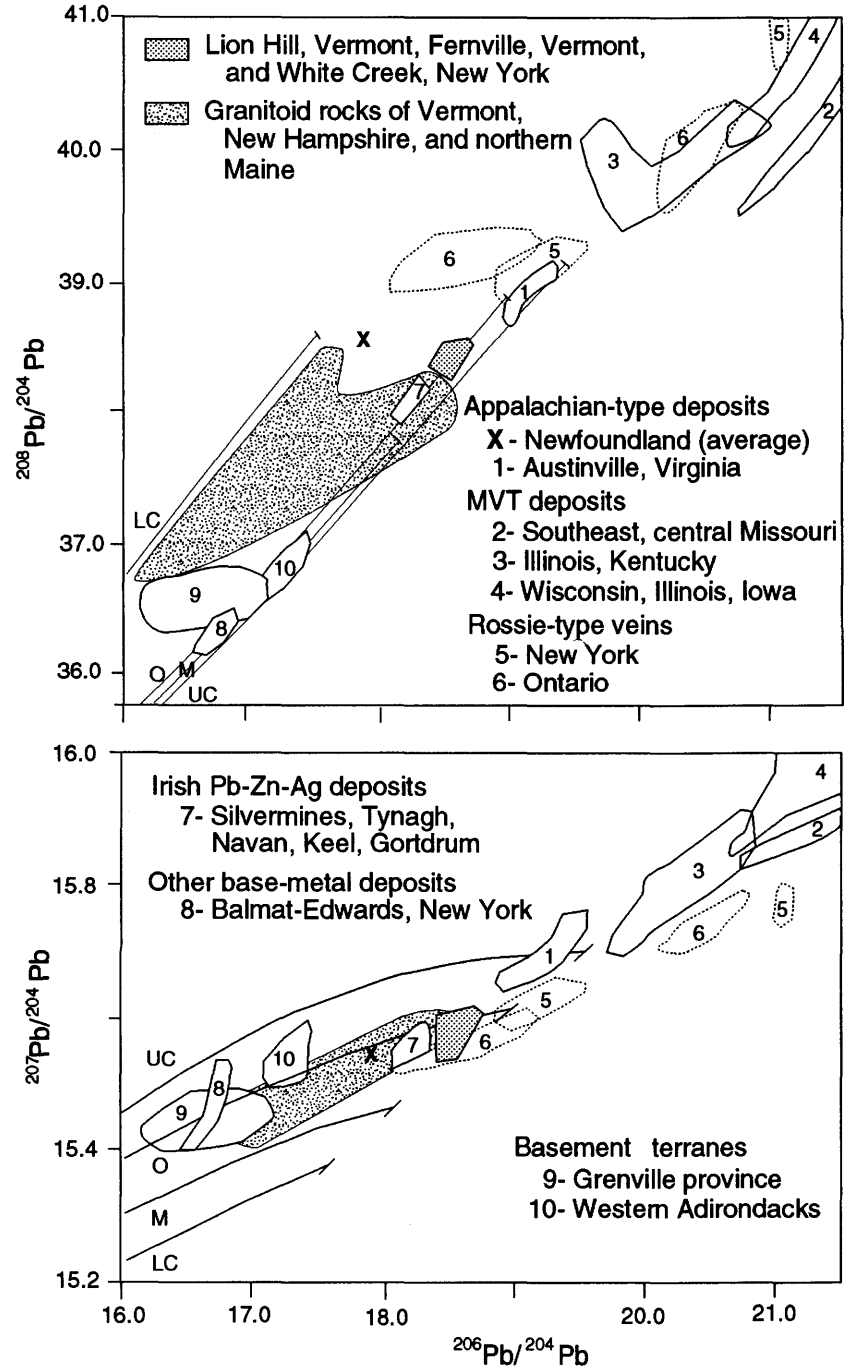


Figure 12. Lead isotopic composition of carbonate-siliciclastic-hosted Pb-Zn minerals from the Lion Hill area, Vt., and White Creek, N.Y., compared to data for similar deposits in Ireland (Silvermines, Tynagh, Navan, Keel, and Gortdrum deposits; Caulfield and others, 1986). Fields are also shown for an Appalachian-type Zn-Pb deposit at Austinville, Va. (Foley and others, 1981), Rossie-type Pb-Zn veins of northwestern New York State (Ayuso and others, 1987) and southwestern Ontario (Fletcher and Farquhar, 1982a), Mississippi Valley-type (MVT) deposits including the southeast and central Missouri Pb-Zn district (Doe and Delevaux, 1972) and the Illinois-Kentucky and Tri-State areas (Heyl and others, 1966), and the Balmat-Edwards district (Doe, 1962; Fletcher and Farquhar, 1982b); an average point is shown for carbonate-hosted deposits of Newfoundland (Swinden and others, 1988). Uncorrected feldspar lead isotopic data for the ~1 Ga Grenville province and the western Adirondack massif are from Zartman and Wasserburg (1969). Age-corrected feldspar data for some granitoid rocks dated at 400 Ma of the northern Appalachians of the United States and Canada are from Ayuso (1986) and Ayuso and Bevier (1991). Curves on both plots are the average lead environments of Doe and Zartman (1979). M, mantle; O, orogene; UC, upper crust; LC, lower crust.

the seawater-sediment interface, then the fluid-inclusion data for Lion Hill suggest that the mineralizing environment was more like that of Irish-type sedimentary-exhalative deposits than MVT deposits. If the discordant veins formed instead by remobilization of pre-existing sulfide minerals during the Taconic orogeny, then the data cannot be used to distinguish either an MVT or a sedimentary-exhalative (sedex)-type precursor.

Sulfur isotopic values for Appalachian deposits, Irish sediment-hosted base-metal deposits, and for MVT deposits are shown for comparison in figure 13. In general, the Irish-type deposits and Lion Hill have sulfur isotopic compositions with lower $\delta^{34}S$ values, indicating a larger kinetic fractionation factor between sulfate and sulfide relative to most MVT deposits. One of the factors controlling kinetic fractionation is the rate of bacterial reduction, which is partly dependent upon the amount of organic material. The difference in kinetic fractionation between the two deposit types may be related to amount of organic material and, thus, may be the result of different depositional processes and environments.

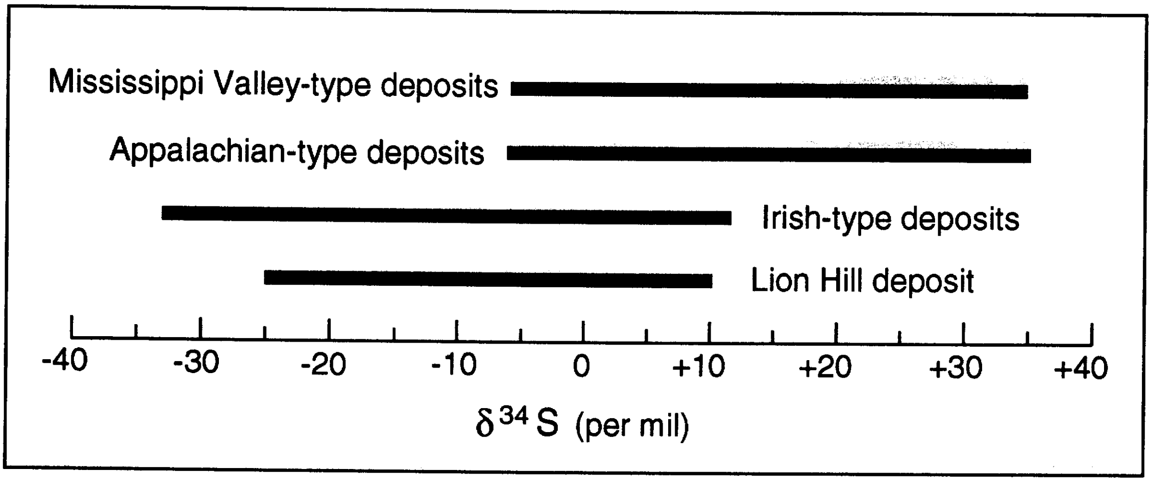


Figure 13. The range of $\delta^{34}S$ for Mississippi Valley-type (MVT), Appalachian-type, and Irish-type deposits compared with data for the Lion Hill deposit. Data compiled from Sangster (1990), Kesler and van der Pluijm (1990), and Caulfield and others (1986).

Lion Hill galenas have lead isotopic compositions that are much less radiogenic than most carbonate-hosted MVT deposits, Appalachian-type deposits, or Rossie-type Pb-Zn-F veins, which are structurally controlled, carbonate-hosted veins that are widespread in the Frontenac axis area of New York and Ontario (Ayuso and others, 1987) (fig. 12). Galenas from Lion Hill also show a much smaller spread in lead isotopic composition compared to these deposit types. The MVT, Appalachian, and Rossie-type veins are characterized by a strong imprint of upper crustal lead, whereas Lion Hill galenas have an average orogene signature.

Stratabound and stratiform deposits of the Selwyn basin have been proposed as a possible analog of the marble and anhydrite-hosted Zn-Pb deposits at Balmat, New York (Whelan and others, 1990), that occur in rocks of the Grenville province of the Adirondack massif. Lead isotopic values of galenas from Balmat are only moderately heterogeneous (Doe, 1962). Lion Hill galenas differ from Balmat galenas in that Lion Hill galenas have relatively lower $^{207}Pb/^{204}Pb$ values, again suggesting that any involvement of a component of upper crustal lead in the formation of the Lion Hill galenas was limited.

Compared to galenas from carbonate-hosted Pb-Zn-Ag deposits of Ireland, galenas from the Lion Hill deposit show a similarly moderate spread in lead isotopic composition (fig. 12). Lead isotopic ratios of galenas from individual deposits in Ireland exhibit little heterogeneity, although there are larger differences among deposits (Caulfield and others, 1986). Lead isotopic data for both the Lion Hill galenas and those of the Irish deposits generally follow average-orogene evolution paths (fig. 12), and show only a slight deviation below the average-orogene evolution curve in $^{207}Pb/^{204}Pb$. The general similarity in lead isotopic values between Lion Hill and carbonate-hosted Pb-Zn-Ag deposits of Ireland may indicate that the source rocks for these deposits had overlapping lead isotopic signatures and, also, that the processes operating to extract lead from source rocks of Lion Hill were akin to those that formed the Irish deposits.

GENETIC MODELS

Genetic models considered for the Lion Hill deposit included sedex and diagenetic (Briskey, 1986; Hitzman and Large, 1986; Sangster, 1990), Mississippi Valley-type (Briskey, 1986; Kesler and van der Pluijm, 1990; Sangster, 1990), and Appalachian zinc (Briskey, 1986; Foley and others, 1981). Although the Lion Hill deposit resembles many Zn-Pb deposits that are classified as MVT- and Appalachian-type deposits in general aspects (for example, carbonate host rock, vein structures, low temperature, and moderately saline fluid regime), a detailed analysis suggests that the Lion Hill deposit is more closely analogous to the sediment-hosted base-metal deposits of Ireland (Navan, Tynagh, Silvermines).

Many Pb-Zn-Ag deposits of Ireland, including Tynagh, Silvermines, and Keel, that were once thought to be sedex or early diagenetic in origin are now considered to have formed in a diagenetic to epigenetic setting (Taylor, 1984; Briskey, 1986; Samson and Russell, 1987; Ashton and others, 1992; Hitzman and others, 1992). Russell and others (1982) proposed a sedex origin for the Irish deposits, while others, such as Hutchinson (1983), suggested that the ores were actually epigenetic. Taylor and Andrew (1978) suggested a hybrid model for the origin of the Silvermines deposit in which stratigraphically lower epigenetic ores were deposited in a feeder zone and upper ores were deposited syngenetically from exhalations near the sediment-seawater interface. Caulfield and others (1986) applied this hybrid model to the epigenetic ores at the Keel deposit and stressed the dependence of syngenetic, diagenetic, and epigenetic processes of ore deposition on the rate of fluid expulsion and on local geologic controls. More recently, Ashton and others (1992) presented a model for the Navan deposit that incorporates diagenetic and epigenetic styles of mineralization. Some important characteristics that are shared by most Irish models include the following (M. Hitzman, National Science Foundation, written commun., 1994): (1) the metals occur in stratigraphically low, nonargillaceous carbonate units, (2) the mineralized zones are near major structures available to serve as conduits for fluids, (3) in general the temperatures of deposition are >175° to >150°C, (4) wallrock alteration includes extensive dolomitization, (5) many of the sulfides formed by replacement and colloform banding is common, (6) the bulk sulfur source was probably Carboniferous seawater sulfate; minor amounts of deep-seated sulfur may occur in feeder zones, (7) mineralization occurred during a period of tectonic instability, so the carbonate shelf rocks are faulted and the local stratigraphic sequence indicates a complex facies mosaic of shallow- and deep-water environments.

As noted above, the apparent overthickened stratigraphic sequence in the vicinity of Lion Hill suggests a remote possibility that growth faults were a factor in transporting fluids to depositional sites at Lion Hill. Current theories about the nature of mineralizing fluids in sedex deposits favor slightly acidic brines that are generated in clastic-dominated sedimentary basins (Lydon, 1983, 1986; Sangster, 1990). Metals leached in the transformation of clay minerals during burial and compaction (Lydon, 1983, 1986) or by deeply circulating fluids (Russell, 1986) are thought to be transported, possibly along growth faults, to depositional sites near or on the sea floor. Growth faults have been identified in Cambrian shelf rocks of western and north-central Pennsylvania and east-central Kentucky (Wagner, 1976; Beardsley and Cable, 1983) and in carbonate shelf rocks north of Burlington, Vt. (R.W. Beardsley, University of Vermont, oral commun., 1992), and in west-central Vermont (Rowley, 1982).

The magnetite iron formation at Lion Hill may have formed from local exhalation of solutions that precipitated iron and associated minerals in a local basin. The presence of iron formation at Lion Hill indicates that iron-mineralizing fluids may have reached the sea floor, at least locally, and that some galena and other sulfide minerals were deposited syngenetically. Iron formation at Tynagh, Ireland (Boast and others, 1981; Clifford and others, 1986), was also thought to have formed by syngenetic exhalation; however, recent work suggests that the iron formation cuts across stratigraphy and is diagenetic. Studies are currently underway to address this question at Tynagh (M. Hitzman, National Science Foundation, written commun., 1994).

Pb-Zn-Cu sulfides may have precipitated from warm, metal-bearing brines that migrated through poorly consolidated sediments near the seawater-sediment interface. The temperature-salinity relationships for fluid inclusions from Lion Hill (and for Silvermines and other Irish-type deposits) are consistent with such a model because they suggest that water (or water + sediment) depths of 50–150 m would have been required to prevent boiling of the hottest hydrothermal fluids in a sedex environment. The bulk of the sulfur isotopic data indicate that the system was relatively open to influx of seawater during the main interval of mineralization; however, closed-system behavior, typical of tidal basins and seawater trapped as pore fluid in wet sediments, was also an important control on the sulfur isotopic composition of some sulfides.

Localization of metal-bearing brines may have been caused by variations in porosity and permeability, with reduction-oxidation (redox) differences providing a mechanism for early diagenetic precipitation of sulfide minerals. Other possible mechanisms for precipitation include fluid mixing, pH change, conduction, and so forth. Because the host rocks of the Lion Hill deposits may have formed as tidal-flat sediments (in contrast to Irish-type deposits), studies of variations in porosity and permeability in modern tidal flats provide evidence for possible routes for fluid migration and suggest favorable sites for sulfide precipitation. Studies of ancient and modern tidal flats have shown that porosity and permeability of different facies vary greatly; porosity and permeability are best developed in the subtidal to intertidal facies (typically composed of more permeable, coarser grained carbonate), especially in tidal channels, whereas supratidal sediments, composed of fine-grained undisturbed muds, generally have low porosity and permeability (Shinn, 1983). Trap rocks are created by transgressions and regressions that cause intertidal and channel facies to pinch out beneath and within the relatively impermeable supratidal facies. Hydrothermal solutions moving through such permeable zones could be trapped at barriers formed by the supratidal facies. Sediments of the supratidal and upper intertidal zones characteristically are brown and oxidized relative to the gray and more reduced, lower intertidal to subtidal dolomites (Shinn, 1983), and this difference creates potential for sulfide precipitation at a redox interface. These sedimentation facies may account for the apparent displacement of the iron formation at Lion Hill away from the bulk of the base-metal sulfides, because they allow for development of parallel facies of iron formation, as conceptualized by James (1954).

The occurrence of Zn, Pb, and Cu values for Lion Hill rocks in mixed carbonate-siliciclastic rocks, at or above prominent well-sorted siliciclastic units (fig. 8), suggests that the siliciclastic units may have acted as high-porosity and high-permeability pathways for transport of mineralizing fluids, which then were precipitated in the less permeable overlying mixed-carbonate and siliciclastic material. The occurrence of mineralized zones in siliciclastic and mixed-carbonate-siliciclastic sequences at approximately the same depth as weakly mineralized carbonate layers suggests lateral migration of fluids from high-porosity pathways to sites of deposition in adjacent, less permeable lithofacies.

The possibility of an Irish-type origin for some Zn-Pb deposits of the Paleozoic shelf of eastern North America is of considerable significance for improving our understanding of basin evolution, of the timing of mineralization relative to platform evolution, and of the mineral resource potential of the region. The petrologic, geochemical, and isotopic data presented in this report support a sedex model incorporating diagenetic and epigenetic processes for the Lion Hill, Vt., Pb-Zn mineralization—a model akin to that proposed for economically important sediment-hosted Pb-Zn-Ag deposits of Ireland. We believe that a high potential exists for discoveries of a number of additional stratiform Pb and Zn sulfide lenses hosted by the lower Paleozoic platform sequence rocks of western Vermont, as suggested by Clark (1990) and Slack (1990). The economic viability of such deposits at present will depend, however, on whether or not they contain enough Cu and Ag to offset mining and environmental costs of developing the ore bodies. At the present time, the apparent geochemical differences between stratiform sulfide deposits such as those at Lion Hill and at Silvermines or Navan (Zn+Pb±Cu versus Zn+Pb±Cu±Ag) and the size of the mineralized horizons result in grossly different economic potentials. This difference probably reflects the ultimate control of source rock on metallogeny.

CONCLUSIONS

The following elements summarize observations in support of our interpretation of the mineralized rock at Lion Hill as being of the class of deposits that include the carbonate-hosted deposits of Ireland.

1. Sulfide bodies of the Lion Hill deposit include both stratabound and stratiform mineralization. Textural evidence suggests that mineralizing fluids permeated the sediments prior to lithification. Some of the discordant veins at Lion Hill may constitute a feeder zone, while others may have formed in a dilatant mineralized fracture zone soon after precipitation, when the sediments were in a semiconsolidated state.
2. The association of layered magnetite iron formation containing base-metal sulfide minerals with the Zn-Pb-Cu deposit provides possible lithologic evidence for mineralization by submarine exhalative activity. We are unable constrain the timing of this activity; it was probably syngenetic or diagenetic but may have been epigenetic.
3. Sand bars and tidal channels present in the sedimentary section could have acted as relatively permeable pathways for movement of mineralizing fluids. Pinching out of these pathways and the presence of less permeable mixed carbonate and siliciclastic layers in intertidal and supratidal sediments may have created trap rocks that localized sulfide deposition.
4. Homogenization temperatures of primary and secondary inclusions in sphalerite range from 152°C to 196°C, and salinities range from 11.5 to 14.0 wt% NaCl equivalent. These values fall within the ranges expected for some Irish-type deposits; however, they also may reflect metamorphic remobilization of precursor sulfides.
5. The range of $\delta^{34}S$ values for sulfide minerals from Lion Hill, from –25.9 to +10.0‰, falls within the range expected for sulfide produced from bacteriogenic reduction of sulfate with $\delta^{34}S$ values of 25 to 30‰. In addition, some pyrite probably formed from sulfate in trapped pore fluid, resulting in more closed-system behavior and subsequently heavier sulfur isotopic values. Three sphalerite samples with heavier sulfur isotopic values may reflect a change in the source of sulfur, perhaps to deep-seated sulfur, during a later episode of mineralization.
6. The lead isotopic compositions of galena from Lion Hill indicate that Grenville basement rocks and (or) their sedimentary equivalents probably impose the strongest constraint on lead isotopic signature for the mineralization, although the host carbonate-siliciclastic rocks may constitute a secondary source of lead.
7. Fluid-inclusion and sulfur and lead isotopic data for the Lion Hill deposit may support an origin like that of the Irish-type deposits, rather than MVT or Appalachian Zn-type deposits.
8. Our study of the Lion Hill deposit suggests a potential for Irish-type Pb-Zn deposits in platform rocks of western Vermont.

APPENDIX A. ANALYTICAL TECHNIQUES

Chemical analyses were made of samples selected from 9 of 38 drillcores based on detailed logs prepared by J. M. Hammarstrom and E-an Zen (unpub. data, 1972) and by S.H.B. Clark (unpub. data, 1985). Each sample is representative of a core interval of 3 m or less to coincide with lithologic changes. Cores were split and chip samples taken along the entire interval. Most samples were analyzed by inductively coupled plasma-atomic emission spectroscopy (ICP–AES); selected samples also were examined by semiquantitative optical emission spectroscopy (SOES) and (or) quantitative atomic absorption (AA). For the ICP–AES analyses, a partial digestion procedure was used to enhance the detection of ore-related metals and to depress the influence of metals that may reside in the lattices of silicates and sulfates (Mosier and Motooka, 1983). The dissolution procedure completely digests carbonate, sulfide, and iron oxide minerals, although the lattices of most sulfate and silicate minerals are not affected significantly. Samples were digested in 6*N* nitric acid, and then gently dried with low heat and allowed to cool. They were redissolved in HCl (20%) on a warm hotplate and then filtered through paper and analyzed. The partial digestion ICP–AES method is an alternative to time-consuming preconcentration procedures for the detection of metal abundances that are too low to show meaningful patterns from whole-rock samples. In the present investigation, the ICP–AES method was utilized because of its precision. The results enable detection of element distribution patterns that can be related to distinct stratigraphic intervals. SOES and AA techniques followed standard analytical methods outlined in Baedecker (1987).

Mineral separates of sphalerite, galena, chalcopyrite, and pyrite were hand picked for sulfur isotopic analysis from samples of drillcore from the northern and southern areas of the Lion Hill deposit, from the Fernville mine, and from the White Creek deposit. A sulfide concentration (galena + sphalerite + chalcopyrite) was made from magnetite iron formation from the Nicklaw mine. Sulfide separates were converted to SO_2 by roasting with Cu_2O; galena and sphalerite were held at 1025 °C for 10 min, and pyrite and chalcopyrite at 1,125 °C for 15 min. SO_2 that was produced was purified in a glass vacuum-distillation line. Ratio measurements were made on a Nuclide 6" mass spectrometer at the U.S. Geological Survey in Reston, Va. Analytical precision based on duplicate analyses of samples is about ±0.1‰ (1 standard deviation).

Galena crystals 0.1 to 1.0 mm on edge were separated for lead isotopic analysis from samples of drillcore that had been cleaned in distilled water in an ultrasonic bath. The crystals were acid-washed in a 7*N* HNO_3 solution, dissolved in 14*N* HNO_3, and then precipitated as lead nitrate. After drying on a hot plate, the samples were loaded on rhenium filaments by using the silica gel-phosphoric acid technique (Cameron and others, 1969) and analyzed on a 12-in-radius, NBS-type solid-source mass spectrometer. Instrumental fractionation was corrected by comparison of repeat analyses of NBS SRM–982. All errors are reported as standard error of the mean at the two-sigma level and are generally <0.15 % (2σ) of the measured ratios.

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