Paleokarst and Associated Mineralization at the Linwood Mine, Scott County Iowa

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Operations at the Linwood Mine in Scott County, Iowa, have exposed, on two working levels, extensive pre-Pennsylvanian paleokarst and associated sediment fillings and mineralization in Middle Devonian limestones. Cavities in Davenport-Spring Grove host rocks range up to 270 meters in length and are virtually all filled with fluviatile sediment. Cavities in Cedar Rapids host rocks, on average, are smaller and some are unfilled. Limestone dissolution was controlled by high-angle fractures with a wide variety of orientations and by bedding plane and stylolitic partings. Dissolutional features on both levels of the mine provide evidence for phreatic and vadose processes. Most of the unfilled cavities in the Cedar Rapids Limestone contain abundant mineralization, which occurs as cavity linings, fracture fillings and fillings, breccia cements and disseminations in sediment fillings and cavity walls. Mineralogically, calcite is dominant, marcasite, barite and pyrite are widespread and locally abundant, sphalerite is uncommon, and chalcopyrite and quartz are rare. Calcite appears in several generations involving alternations between acute and obtuse crystal forms. Barite occurs in a wide variety of habits; multicrystalline barite differs from monocrystalline barite in color and distribution within cavities. Iron sulfide precipitation began early, and continued intermittently throughout the period of the mineralization. Calcite is intermediate to late and barite is late. Distinctive features of mineralization include minerals contained wholly within mudstone, boxwork, and iron sulfide which appears to be stalactitic. Vertically, most of the mineralization occurs in the well-beded lower part of the Cedar Rapids Limestone. Presence or absence of specific minerals, mineral distribution and paragenesis suggest that conditions during karst-filling sedimentation, and mineralization were alternately reducing and oxidizing, but most of the mineralization formed during reducing (phreatic) conditions. Mineralization at Linwood shows similarities and differences when compared to other paleokarst-associated deposits in eastern Iowa. Similarities with main district upper Mississippi Valley zinc-lead deposits include broadly similar paragenesis and similarities in multiple generations of calcite.

INDEX DESCRIPTORS: paleokarst, sulfide mineralization, eastern Iowa

The Linwood Mine, owned and operated by the Linwood Mining and Minerals Corporation, is located on the northern side of the Mississippi River just east of Buffalo in Scott County Iowa (figure 1). The mine's beginnings can be traced back at least to 1897. Linwood commenced operations in 1918, producing limestone from an open cut quarry. Around 1956, because of an increased demand for high-purity limestone, and because excessive overburden covered the favorable rock units, underground mining was begun. Current workings extend over 1200 meters in a generally northward direction from portals set in the face of limestone ledges, which are prominent along the Mississippi River in this area. Limestone is produced by the room-and-pillar method from two working levels that are separated from each other by about 5 meters of rock. Pillars average approximately 9 meters across and are laid out on about 21-meter centers. The underground workings now cover several hundred hectares.

Mine workings on both levels expose extensive paleokarst. Paleokarst is defined here as ancient topography, including caves, which results from the solvent action of aqueous fluids upon carbonate rocks. The origin of the fluids, whether meteoric, hydrothermal or some combination of the two, is not specified. Openings in carbonate host rocks contain fluviatile sediment fillings and, especially on the lower level, mineral linings and fillings. Because of recent exposure by underground mining, and protection from the effects of surface weathering and erosion, paleokarst features are in a generally excellent state of preservation. The purpose of this paper is to: 1) describe the nature and distribution of the paleokarst and the associated mineralization, 2) identify, on the basis of form, mineralogy and paragenesis, possible physical and chemical controls of mineralization, and 3) compare Linwood mineralization to other paleokarst-associated mineralization in eastern Iowa and western Illinois, and to mineralization in the formerly commercial Upper Mississippi Valley Zinc-Lead District. Paleokarst-associated minor occurrences of sulfide-bearing mineral deposits have been reported elsewhere in the general area (Spry and Kutz, 1988; Kutz and Spry, 1989; Garvin et al., 1987; Garvin and Ludvigson, 1988, 1993). Locations of known principle occurrences are shown in figure 1. See also Heyl and West, 1982.

GENERAL GEOLOGY

The Linwood Mine workings expose rocks of the Pinicon Ridge and Otis formations of Eifelian (Middle Devonian) age. Rocks of the overlying Cedar Valley Group (Givetian) are exposed by drilling on the mine property. This same stratigraphic section can be observed at the Lafarge Company quarry, which is located immediately west of

Figure 1. Map showing location of the Linwood Mine and nearby rock quarries in eastern Iowa and western Illinois where paleokarst features can be observed. Structural and stratigraphic data from Bunker et al. (1985).
the mine. Working levels of the mine are in the Cedar Rapids Member of the Otis Formation and in the Davenport and Spring Grove members of the Pinicon Ridge Formation. The Otis Shale separates the two levels, and is exposed in inclines connecting them (figure 2). A more detailed description of the rock units at Linwood is recorded in the core log for Iowa Geological Survey Bureau LMM 1989 Core #1 (IDNR-GSB W-51235) (R.M. McKay, written communication).

**OTIS FORMATION** (Middle Devonian-Eifelian)

The Otis Formation consists of two members, the Coggon and the Cedar Rapids. The top of the Coggon forms the floor of the lower mine level and consists of thick- to medium-bedded dolostone (Witzke et al., 1988). The overlying Cedar Rapids Member can be subdivided into three lithologic units, all limestones. The lowest unit consists of 1 to 2 meters of light gray, thin- to medium-bedded dolostone. The middle unit consists of about 3 meters of very light cream to light brownish-gray lime mudstone. The uppermost unit consists of about 2 meters of dense light gray to light brownish-gray lime mudstone. This unit is poorly to moderately bedded. Brecciation is widespread, with breccia clasts ranging up to 8 cm in diameter. Clasts exhibit varying degrees of chemical alteration and some are rounded, presumably due to chemical corrosion. Green clay is common in void fillings. An organic-rich shale parting rests on top of this unit and forms the ceiling marker for the Otis-level workings (figure 3).

**PINICON RIDGE FORMATION** (Middle Devonian - Eifelian)

**Kenwood Member**

The Kenwood Member is dominantly an argillaceous dolostone, which becomes more calcitic toward the top. The Kenwood is variably laminated, stylolitic and brecciated, and thin laminae contain non-calcareous fine clastics. Disseminated micro-grains of pyrite are abundant in some horizons. This unit is about 4 meters thick.

**Spring Grove Member**

The Spring Grove Member consists of 3 meters of very light cream to very light gray-brown recrystallized limestone. It is abundantly stylolitic and locally laminated, with some laminae containing dark brown organic material.

**Davenport Member**

The Davenport Member consists of very light cream to light brownish gray lime mudstone. It is locally lithographic, stylolitic and abundantly laminated. Stylolitic partings may be closely spaced (< 1cm). A dense, very light cream lime mudstone layer approximately 0.5 m thick is prominent in the upper part, and is laterally traceable throughout the mine. In some areas this unit is the ceiling marker for the upper workings. Solution-collapse breccia, for which the Davenport is well known in eastern Iowa, is locally present but generally inconspicuous at Linwood. Where present, interclastic void fillings commonly contain green clay. The Davenport is about 10 meters thick.

**LITTLE CEDAR FORMATION** (Middle Devonian - Givetian)

**Solon Member**

The Solon Member is a light gray skeletal lime packstone to wackestone. It is abundantly fossiliferous, in contrast to all underlying units exposed at the mine. In the mine workings it is observed only as breakdown clasts contained in paleokarst-filling sediment.

**PENNSYLVANIAN KARST-FILLING SEDIMENTS**

Rocks of the Early Pennsylvanian Caseyville and overlying Middle Pennsylvanian Spoon formations crop out west of the Linwood Mine at Wildcat Den State Park and at the Wyoming Hill roadcut. At the mine, Pennsylvanian rocks are present as fluviatile fillings of paleokarst; the formation(s) are as yet unverified. The rocks consist chiefly of weakly to moderately indurated very light gray sandstones, and light gray to very dark gray siltstones and claysones. In small moist cavities, clay is soft and plastic. The sandstones are cemented to varying degree by quartz and locally by pyrite. Sand grains locally exhibit subhedral quartz overgrowths. Carbonized plant material is widespread in all sediments, but is most conspicuous in the sandstones. Wood fragments up to several centimeters in length, most in varying stages of replacement by pyrite, are common (figure 5).

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**Figure 2.** Generalized sequence of middle Devonian strata and Pennsylvanian karst fill in east-central Iowa. Modified from Bunker et al. (1985).

**Figure 3-5.** Figure 3. Calcite-cemented lowermost and middle units of the Cedar Rapids Member. Note bedding in the lowermost unit and absence of bedding in middle unit. Photo by Mike Bounk. Figure 4. Limestone clasts (lower half; light colored) in mudstone fill; overlain by organic-rich mudstone (upper half). Davenport-Spring Grove level. Figure 5. Slab of well-indurated Pennsylvanian sandstone fill. Dark spots in upper part of slab are carbonized wood fragments. Note laminated mudstone at bottom of slab. Quarter at top center of slab (above arrow) for scale. Cedar Rapids level. Photo by Mark McElhiney.
Larger fills dominated by sandstone commonly contain locally-derived clasts of limestone which are angular to subangular and range up to a half meter or more across (figure 4, 6). The clasts include all Wapsipinicon and Cedar Valley group lithologies. Small (less than 3 cm) clasts of green clay are abundant in fills containing sandstone. Small chert clasts occur locally. Locally on the Davenport-Spring Grove level occur what appear to be angular to rounded clasts of sandstone, indicating displacement of overlying fill material. Finer-grained clastics are commonly laminated, with dark-colored claystones alternating with light-colored siltstones. Clay slickensides are common. Layering in the sediment is very complex, locally exhibiting disharmonic folds, slump features, and cut and fill structures. On the Cedar Rapids level, karst-filling materials in most cavities are dominantly silt- to clay- sized. Where sandstone is present (generally in larger cavities), the cavities are commonly floored and roofed with mudstone which is often laminated.

GREEN SHALE (age unknown)

On both the Cedar Rapids and Davenport-Spring Grove levels of the mine, another karst-filling material occurs. It consists of moderately indurated greenish-gray claystone and siltstone, that is weakly fissile and in part calcareous. It contains scattered rounded quartz sand grains. On exposure to air, small (< 1 cm) gypsum rosettes quickly form on fracture surfaces. Locally, at the bottoms of cavities containing a concentration of limestone clasts, the void-filling material is green shale. Where the two sediments are observed in contact, the green shale is overlain or truncated by dark gray Pennsylvanian shale (figure 7). This relationship clearly indicates that the green shale is older than the Pennsylvanian sediment. It is observed only rarely in quantity, but small clasts are widespread in Pennsylvanian sediment. In addition, where Pennsylvanian sediment has fallen from cavity ceilings during mining operations, green clay is frequently observed coating ceiling rocks. Whether or not this clay belongs to the same generation as that found beneath Pennsylvanian fill material is not known.

PALEOKARST

Karst, both ancient and modern, is widespread in the upper Mississippi Valley. Ancient karst is most readily observed in active limestone quarries, where its existence is often marked by dark, organic-rich sediment fill, and by the concentration of limonite stains, which result from the oxidation of iron sulfide-bearing fill (figure 1). At the Linwood Mine paleokarst is evident in the rocks on both the Davenport-Spring Grove and Cedar Rapids levels. Solutional openings are exposed in pillars and walls on both levels of the mine.

Figure 6. John Ward, holding up ceiling near large cavity on Cedar Rapids level containing mudstone fill with highly altered limestone clasts. Exposure by mining has caused fill to slough away from ceiling. Photo by Mark McElhinney.
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Figure 7. Sketch showing age relations between Pennsylvanian mudstone and green shale.

They range from a few centimeters to more than 200 meters in maximum dimension, with the largest caverns occurring in the Davenport.

Karst can be classified broadly as either holokarst or merokarst (fluviokarst). In holokarst, dissolution of carbonate rock is extensive and drainage is entirely karstic. In merokarst, dissolution is less extensive and drainage is part surface and part karstic (White, 1988). The presence of large interkarst areas at Linwood and the existence of nearby Pennsylvanian fluvial deposits (Wyoming Hill and Wildcat Den) clearly identify Linwood karst as merokarst.

CONTROLLING FACTORS IN KARST DEVELOPMENT

Because of the generally low stratal permeability of carbonate rocks at Linwood, karstification was not pervasive; rather, it was controlled by essentially horizontal bedding plane and stylolitic partings and high-angle fractures. In order to determine the spatial distribution of cavities, more than 2000 cavities exposed on both levels of the mine and their contents were documented using a system of X-Y-Z coordinates to locate the approximate geometric center of each cavity. Cavities less than 0.1 meter in cross-sectional area were considered too small for mapping. Locations of cavity centers were used to construct areal and vertical distribution plots. Cavity characteristics were plotted in order to identify possible patterns of their distribution. These characteristics include presence/absence, size (cross-sectional area), control (bedding plane vs. high-angle fracture, and fracture orientation), general nature of fill material, and, additionally for the Cedar Rapids level, presence or absence of specific minerals and crystal habits. Vertical distribution of cavities and selected attributes (size, control, etc.) was determined as a function of height above the mine floor. The mine floor on the Cedar Rapids level is set at the base of the Cedar Rapids Member (at the top the dolostone). The floor on the Davenport-Spring Grove level is at the top of the Kenwood Shale.

In Cedar Rapids host rocks, dissolution was strongly influenced by differences in the physical character of the three units of the Cedar Rapids Member. This fact can readily be observed in the vertical distribution plot (figure 8). Most of the cavities occur in the well-bedded lowest unit, where dissolution was controlled principally by horizontal partings. These cavities are mainly sediment-filled seams along bedding planes. In the massive, poorly bedded middle unit, high-angle fractures exerted primary control on dissolution. In the brecciated, locally bedded uppermost unit, high-angle fractures, bedding plane and stylolitic partings and areas of collapse brecciation controlled dissolution. The plot reveals that high-angle fracture-controlled cavities are more or less uniformly distributed throughout the Cedar Rapids Member. Vertical distribution of large cavities (cross-sectional area > 5 m²) closely follows that for fracture-controlled cavities, indicating that high-angle fractures were the principal control in large cavity development.

It is difficult to establish an areal pattern of cavity distribution on either level of the mine. As seen on the vertical distribution graph for the Cedar Rapids level (figure 5), the majority of cavities are controlled by horizontal partings. Establishing axes for such cavities is
Figure 10. Distribution of identified high-angle fracture-controlled cavities - Davenport-Spring Grove level. The grid is approximately 300 x 300 m.

difficult because of limited horizontal exposures, and because they tend to be sinuous and curvilinear (Palmer, 1991). Cavities that appear to follow a high-angle fracture often end so abruptly that it is impossible, from a mine floor vantage point, to trace the fracture in the mine ceiling beyond the cavity limits. Cavities which are chimney-shaped and circular in cross-section (these are abundant in the Cedar Rapids Member) generally can not be related to defined fractures, even though chimneys generally are considered to form at fracture intersections. For the numerous small, equidimensional cavities, control could not be determined with certainty.

For those cavities in which development was controlled by high-angle fractures, areal distribution maps and rose diagrams for both levels are shown in figures 9, 10, 11 and 12. In comparing the rose diagram with the areal distribution map for the Davenport-Spring

Figure 11. Rose diagram for identified high-angle fracture-controlled cavities - Cedar Rapids level. The total number of data points is 100.

Figure 12. Rose diagram for identified high-angle fracture-controlled cavities - Davenport-Spring Grove level. The total number of data points is 184.
Grove level (figures 9 and 11), it should be noted that individual cavities, regardless of size, were plotted as single data points, unless the cavity direction changed significantly. Thus the large, nearly E-W cavity west of center was plotted as a single data point, and the long, generally NE-trending cavity east of center was plotted as 4 data points, because of 3 changes in strike of the cavity axis. This latter cavity is clearly controlled by two different fracture sets.

The areal distribution map and the rose diagram for the Cedar Rapids level are shown in figures 10 and 12. Both reveal a strong northeasterly alignment of cavity axes. There appears to be a closer correspondence between the high-angle fracture distribution map and the rose diagram for the Cedar Rapids level than for the Davenport-Spring Grove level. It must be noted, however, that the control for many cavities could not be ascertained because of their equidimensional nature and the general inability to observe and trace fractures in pillar walls and mine ceilings. The long cavity illustrated in the southern part of the map is a narrow sinuous channel exposed in the mine ceiling, the vertical extent of which is no more than 2 meters. This cavity was likely controlled primarily by horizontal partings. The cavities whose orientations could be determined with some degree of accuracy are generally large (>5 m² cross-sectional area). Most of these have northeast-trending axes.

Since there is better fracture definition on the Davenport-Spring Grove level than on the Cedar Rapids level, Davenport-Spring Grove areal plots probably give a more accurate representation of fracture distribution at the Linwood Mine. Superimposing the areal distribution plots for the two levels does little to clarify the picture, largely because of the limited overlap between the mapped workings on the two levels. Even large cavities cannot be traced from one level to the next. Based on mining experience, it is virtually impossible to predict with certainty where cavities will be found in unmined areas. As can be seen on the map, for the most part, openings are short and discontinuous, with a few notable exceptions on the Davenport-Spring Grove level (figure 7).

In the Kenwood Formation, which is a shaley dolomite, cavity development was inhibited both by the low permeability and the relative impermeability of the rock. Thus, the Kenwood makes a stable mine floor for Davenport-Spring Grove workings and a stable ceiling for the underlying Cedar Rapids workings.

CAVITY MORPHOLOGY

The morphology of cavities exposed at Linwood is variable and complex. Identifying the horizontal and transverse shapes of individual cavities is difficult for two reasons. First, a portion of the original cavity may have been removed during mining. In several localities on the Cedar Rapids level large (>1 meter across) breakdown blocks litter the floor of the rooms, but little evidence of cave walls can be found in the surrounding pillars or the ceiling. These caves, though large enough to accumulate large breakdown, were smaller than the rooms. Second, the majority of the cavities, especially in Davenport-Spring Grove host rocks, are completely filled with sediment. Where a cave is exposed in the surface of a pillar or wall, only a two-dimensional cross-section is presented to view. The angle of cross-section in relation to the axis of the cavity cannot generally be determined, unless the cavity is large enough to extend into the ceiling of the adjacent room. In the case of large sediment-filled caves the ceilings of which extend above the mine ceiling (rooms range in height from 7 to 11 meters), when the caves are exposed during mining, the sediment fill progressively sloughs out to the floor. The result is a conical or ridge-shaped pile of sediment that may be as much as 5-6 meters high. These piles permit observation of the morphology of cavern ceilings and walls from vantage points high above the mine floor.

Elliptical tubes

Cavities controlled chiefly by bedding plane or stylolitic partings are elliptical in cross section. This type is common in the lower unit of the Cedar Rapids Member, where ellipse heights are generally less than 2 meters and widths may be as much as several meters. Sediment fillings along bedding plane partings may thin to as little as a few centimeters. Upper surfaces of ellipses may be more steeply arched than lower surfaces. This asymmetry suggests water-filled cavities in which corrosion was more rapid upward. Larger elliptical tubes are common in the upper part of the Cedar Rapids, and they occur locally in the Davenport-Spring Grove. Upward arching of large ellipses in some places results from collapse of roof rock (figure 15). Where observed extending into ceilings, elliptical tubes are circular or elliptical in plan view. The axis of the ellipse generally identifies the direction of a controlling fracture. Elliptical tubes are believed to form as groundwater flows along bedding planes under pipe-full (phreatic) conditions (White, 1988; Palmer, 1991).

Angular passages

Where horizontal partings and high-angle fractures intersect, groundwater dissolution may produce stair-step-shaped passages. These are developed on a small scale in the lower Cedar Rapids, where cavity heights and steps are generally less than 1 meter. All observed examples are completely sediment filled. Their development in flat-lying carbonate rocks suggests a steep hydraulic gradient, where groundwater flow is downward, alternating between fracture types (White, 1988).

Canyons

Canyons are vertical to near-vertical passages with widths which are narrow in comparison to their heights. These are observed best in the Davenport-Spring Grove, where they may appear in the ceiling and extend to varying distances down into adjacent pillars. All observed examples are generally a meter or less in width, and almost all are completely sediment-filled (figure 14). Canyons may result from the downward-cutting of a free flowing stream during lowering of base level, or they may form by dissolution of walls along a completely water-filled fracture (White, 1988; Palmer, 1991).

Chimneys (Shafts)

Chimneys, like elliptical tubes, are circular to elliptical in plan, but they are much higher than they are wide. Common in the Cedar Rapids, chimneys generally are widest in the uppermost unit, narrow to very narrow in the middle unit, and widening again in the lowest unit. They are generally barren of Pennsylvania sediment, but may contain altered green shale in voids among breakdown (figure 16). Chimneys are considered to result from the solvent action of groundwater along the intersection of two or more vertical fractures (White, 1988; Palmer, 1991). At Linwood controlling fractures are generally inconspicuous.

Sinuous Channels

Incised into the ceilings of the mine on both levels are sinuous channels. Channel widths rarely exceed a half meter; lengths range upwards from a few meters (figure 15). One continuous channel on the Cedar Rapids level can be traced for 300 meters. They appear as inverted small meandering stream channels, and are typically filled with sediment. Sinuosity does not appear to be controlled by fractures. Where channels pass into pillars, they generally wedge out within 1 to 2 meters below the ceiling. Sinuous channels are likely controlled by horizontal partings (Palmer, 1991). Similar appearing channels, observed in the ceilings of some sinuous caves, are believed to result from upward cutting due to aggradation of sediment on the channel floor (Bretz, 1942).
Complex Forms

On the Davenport-Spring Grove level some large linear to sinuous caves have diamond-shaped or triangular cross-sections. The upper part of the diamond is like a Gothic arch, with the apex containing the controlling fracture. Where free of sediment fill, cave walls reveal vertical flutes and scallops. The diamond shape is probably the result of downward cutting along a high-angle fracture and widening along a horizontal parting. The triangular-shaped cavities are typically floored at the top of the white marker bed, which apparently served as an aquiclude. Some elliptical tubes have canyons incised in their floors, suggesting a change from phreatic to vadose conditions of cavity formation (figure 17).

Figure 13-16. Figure 13. Filled elliptical tube arched by breakdown, filled with laminated mudstone - Cedar Rapids level. Photo by Mark McElhinney. Figure 14. High-angle fracture controlled canyon filled with mudstone - Cedar Rapids level. Width of photo is about 1.5 meters. Photo by Mark McElhinney. Figure 15. View from mine floor of ceiling channel - Davenport-Spring Grove level. Fill material has fallen out. Width of photo is about 4 m. Photo by Mike Bounk. Figure 16. Mineralized chimney - Cedar Rapids level. Norm Nondorf at right.
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Figure 17-19. Figure 17. Elliptical tube with canyon in floor filled with laminated mudstone - Cedar Rapids level. Outlined in ink. Width of photo is about 1.5 m. Photo by Mark McElhiney. Figure 18. Mineralized breakdown blocks in unfilled cavity - Cedar Rapids level. Width of photo is about 1.5 m. Photo by Mark McElhiney. Figure 19. Small high-angle fracture controlled cavity containing large euhedral calcite crystals - Cedar Rapids level. Photo by Mark McElhiney.
KARST FILLING MATERIALS

The majority of the cavities in the carbonate rocks at Linwood are sediment filled. Unfilled cavities are rare on the Davenport-Spring Grove level. On the Cedar Rapids level some small unfilled cavities are floored with organic-rich mudstone. Sealing of conduits by sediment and perhaps mineral cements during early stages of filling kept some cavities largely sediment free. At one locality on the Cedar Rapids level, a large elliptical tube directly overlies another of similar dimensions. The upper cave is completely filled with sediment, while the lower one contains only ceiling breakdown, despite the fact that the two caves are separated by only a half meter of rock.

Karst filling materials consist primarily of local breakdown, Pennsylvanian fluviatile sediments and green shale. The lithologies of the filling materials were described previously. It is important to point out that breakdown clasts, especially in caves on the Cedar Rapids level, are in many cases highly altered. In some places limestone may be so severely altered that it physically appears clay-like; in others, limestone exhibits little, if any, signs of alteration (figure 6). Green clay clasts are variably stained by limonite.

Some of the clay-sized fill material could be insoluble residue from the dissolution of carbonate rock; however, the relative contribution from this source at Linwood is probably minor, owing to the relative purity of Davenport and Cedar Rapids limestones.

MINERALIZATION

GENERAL DISTRIBUTION

Mineralization, though occurring on both levels of the mine, is much more abundant on the Cedar Rapids level, primarily because space for mineral growth is much greater in unfilled cavities in Cedar Rapids rocks. Minerals occur as cavity linings, fracture linings and fillings, boxwork, limestone breccia cements, and disseminations and concretionary growths in paleokarst sediment fills (figures 18-20).

MINERALOGY

Calcite

Calcite is by far the most abundant mineral in Cedar Rapids host rocks. Early (pre-Pennsylvanian) calcite lines bedding-plane fractures in the lower unit, and small cavities, vertical joints and crckle breccia voids in the middle unit (figures 21 and 22). Pre-Pennsylvanian calcite is typically a coarse druse, consisting of simple scalenohedra, with individual crystals typically a centimeter or less in length. Pre-Pennsylvanian calcite is colorless in visible light and creamy yellow to white in long wave (λ=356 nm) ultraviolet light (UV). Crystal faces are always etched (figure 22).
Later (post-Pennsylvanian) calcite is most abundant as linings of cavity ceilings, floors and walls. It also coats surfaces of, and locally cements, breakdown clasts. Crystal forms are complex and typically involve combinations of acute (elongated with respect to the c-axis) and obtuse (flattened with respect to the c-axis) scalenohedra and rhombohedra. Individual acute scalenohedra up to 20 cm in length and obtuse scalenohedra up to 12 cm across have been observed. Phantoms are common, involving both early acute/late obtuse and early obtuse/late acute growth relations. Phantoms are highlighted by dustings of microscopic iron sulfide on interior growth surfaces.

Two phantoms (indicating three growth episodes) within an individual crystal have been observed. Rhombohedral and rare basal twins occur locally. Cavity-lining calcite is transparent to translucent, colorless to pale yellow in visible light and orange pink to dull violet in long-wave UV (figures 22-30). Calcite locally shows etching, which may be crystal form-specific or crystal orientation-specific.

Calcite also occurs as linings and fillings of fractures that extend into the host rock from cavity walls. Where present, crystal forms and colors are similar to those for calcite lining cavities. This type also occurs, albeit uncommonly, on the Davenport-Spring Grove level.

Locally, calcite crystals are found on mud-coated floors of small cavities. Crystals are doubly terminated and may be simple acute scalenohedra or more complex forms ranging up to 6 cm in length. Rarely, colorless, nonfluorescent calcite is found wholly within cavity-filling mud. The presence of doubly terminated crystals, indicates that nucleation occurred within the mud (figure 31).

Boxwork, in which calcite is the main structural material, is locally important on the Cedar Rapids level, where it is most often associated with chimneys. It consists of microcrystalline to sparry calcite cores overgrown with more coarsely crystalline calcite and minor marcasite. Light green or brown clay (pre-Pennsylvanian) may be present in sheltered voids. Boxwork may be attached to cave walls or, more commonly, may occur as "nests" of loose masses which are separated by altered limestone or clay. The deeper into the nest one digs, the more interstitial altered material one finds (figures 32 and 33).

Significantly, ancient vadose speleal calcite has not been observed at Linwood. However, calcite dripstone and flowstone are currently forming at two or three localities near the west end of the Davenport-Spring Grove workings. Here, meteoric water cascading from the ceilings of large caverns is precipitating microcrystalline calcite on cave walls, breakdown and mine floor rubble. Precipitation on floor rubble provides evidence that deposition began after the workings were opened (about fifteen years ago). Thicknesses of as much as one centimeter of dripstone have precipitated during that short period of time!

Barite is widespread and locally abundant in rocks at the Cedar Rapids level, but rare in rocks at the Davenport-Spring Grove level. It occurs in a variety of habits, with individual crystals typically tabular to prismatic. Multi-crystal habits include plumose aggregates, rosettes, druses and rare stalactites. Multicrystalline barite is typically found on ceilings and overhanging walls, while monocrystalline barite occurs on floors, in mud fillings, or in altered breakdown. All multicrystalline barite fluoresces creamy white to white in long-wave UV, whereas all monocrystalline barite is non-fluorescent (figures 34-40).

Plumose barite occurs principally in the western and central parts of the Cedar Rapids level. It most often occurs in elliptical tubes or chimneys and is restricted to cavity ceilings and overhanging walls. The plumes are subparallel aggregates of tabular crystals, and individual plumes may reach 8 cm in length. Plumose barite ranges in color from creamy white to amber (figure 34).

Barite rosettes are widespread throughout the Cedar Rapids level of the mine. They consist of randomly- to subparallel-oriented bundles of tabular crystals, which in some cases are wafer thin. Rosettes may be sparsely scattered or in thick clusters. They range in color from opaque creamy white to translucent dark amber. Locally, subparallel aggregates of lustrous tabular crystals appear micaeous (figure 35-36).

Stalactitic barite was observed at one locality. Perched on the ceiling of a breakdown-modified elliptical tube, the stalactites are not more than 2 cm in length. They consist of an aggregate of barite microcrystals around hollow centers. Barite stalactites are intimately associated with plumose barite. Single barite prisms occur principally in the northern and central areas of the Cedar Rapids level. They are virtually restricted to the middle unit and occur on the floors of small (less than 0.1 m² in cross-sectional area) sediment-free cavities lined with acute scalenohedral calcite. Most often the cavity contains a solitairystal, which may reach 3 cm in length. Color ranges from pale to golden yellow (figure 37).

Monocrystalline barite also occurs in cavities containing Pennsylvanian mud floors or fillings. On floors the barite is generally euhedral, with individual crystals ranging up to 9 x 12 cm. In at least one case it is obvious that the barite grew directly on mud, because it extends into a desiccation crack. Rare occurrences of this type are found on the Davenport-Spring Grove level. Barite occurring in mud-filled cavities also occurs as large prisms (up to 10 cm in length), but the growth surfaces are generally rough, exhibiting low to very high relief (figure 38). Barite of this type is colorless to golden yellow. Observed in a single sample of soft gray clay were tiny tabular crystals of barite, which clearly nucleated within the clay.

In two widely-separated localities monocrystalline barite was found in breakdown containing highly altered limestone and partially oxidized green clay. At both sites barite occurs as complex prismatic crystals that are frequently intergrown. Maximum crystal length is 9 cm, and color ranges from colorless to dark greenish gray. Late growth [h01] faces fluoresce creamy white; otherwise, this barite, as all other prismatic barites, is non-fluorescent (figure 39).

Barite occurs locally as a fine druse, dusting post-Pennsylvanian calcite crystals and boxwork (figure 40).

Pyrite is generally inconspicuous at Linwood, occurring chiefly as microscopic inclusions in calcite and barite. It occurs locally on the Cedar Rapids level as encrustations of microcrystals and small macrocrystals on host rocks. In some places, encrustations have broken free from walls, and have been subsequently cemented with anhedral calcite spar or bladed marcasite overgrowths (figure 37).
Pyrite also forms the inner parts of stalactitic-appearing masses, the origin of which will be considered later (figure 42-43). Typical crystal forms are octahedron and cubo-octahedron. Pyrite is widely disseminated in paleokarst-filling sediments. In green shale it appears as scattered micrograins; in organic-rich Pennsylvanian mudstone it is disseminated or concentrated along bedding planes. In sandstone it locally cements quartz sand grains, is concentrated in concretionary masses as much as several centimeters across and replaces carbonized woody plant material. In fact, most carbonized plant material appears to be variably replaced by pyrite. Upon exposure to mine air, unstable pyrite in karst-filling sediments quickly oxidizes, resulting in limonitic stains on pillar and heading surfaces.

Pyrite is frequently concentrated in the ceiling or hanging wall of carbonate host rocks immediately adjacent to sediment-filled cavities, particularly if the sediment in contact with the host rock is organic-rich mudstone. This relationship is widely observed in carbonated-hosted sediment-filled cavities in eastern Iowa (Garvin et al., 1987; Garvin and Ludvigson, 1993).

Marcasite

Marcasite, like calcite, is widespread, occurring in virtually every mineralized cavity on both Cedar Rapids and Davenport-Spring Grove level. It occurs as coatings or scattered individual crystals or crystal clusters on earlier mineral or host rock surfaces (figures 20 and 44). It is also very common as microscopic inclusions in calcite. Crystal habits are typical for minor sulfide-bearing occurrences in eastern Iowa and include single blades and wedges, complex twins and intergrowths, rosettes and rare acicular forms. In cavities with mudstone floors marcasite forms wafer-thin sheets of microcrystals along horizontal partings.

Sphalerite

Sphalerite is a minor mineral at Linwood. Where observed, it generally fills fractures in limestone or replaces hanging-wall limestone immediately adjacent to sediment-filled cavities on both the Davenport-Spring Grove and Cedar Rapids levels. A large (3 cm across) crystal was extracted from mud in a small filled cavity on the Cedar Rapids level. The cavity also contained calcite and marcasite. Sphalerite is the dominant mineral in a small small (cross-sectional area = 0.4 square meters) cavity in the southern part of the Cedar Rapids level, where it occurs as loose clusters of crystals a centimeter or more across (figure 45). The crystals are etched and exhibit polyhedral twinning. All sphalerite observed at Linwood is macrocrystalline and dark brown in color. Color banding is in conspicuous.

Miscellaneous Minerals

Chalcopyrite was observed in two or three localities on the Cedar Rapids level. Crystals are microtetrakaidecahedron and are included in, and scattered on, post-Pennsylvanian calcite.

Crystalline quartz occurs in two or three localities on the Cedar Rapids level as small, randomly-oriented anhedral to microcrystalline crystals that appear to replace partially pyritized mudstone.

Dolomite rhombs were observed on a single sample from the Cedar Rapids level. About 2 mm across, they formed on a cavity in dolostone host rock. This sample was taken from low in a pillar and may be from the underlying Coggon Member of the Otis Formation.

Several sulfates, including gypsum, melanterite, and roseneite occur on fracture surfaces in paleokarst-filling mudstone. These sulfates most likely result from the alteration of iron sulfides by exposure to air during mining operations. Melanterite exhibits short fibrous crystals which are bright blue in color. Upon removal from the humid atmosphere of the mine, it quickly alters to roseneite.

PARAGENESIS

The first events of significance to the mineralization at Linwood, following the deposition of the host carbonate rock, involve host rock dissolution. Three periods of extensive carbonate dissolution are recognized at Linwood. In the first, stratal dissolution of evaporite units within the Davenport occurred, the process likely beginning during the open marine deposition of the lower Cedar Valley Group (Witzke et al., 1988). Extensive solution collapse of the Davenport and overlying Solon produced widespread brecciation. Davenport breccia at Linwood is more localized than in the areas to the west.

Following the deposition of the rocks of the Wapsipinicon and Cedar Valley groups, carbonate rocks of the area were subjected to a second period of dissolution and karstification. What now appears as green shale was deposited in solution cavities. The absence of large green shale fills indicates that 1) solution cavities were small, 2) large cavities were not completely filled, or 3) some green shale was subsequently removed.

A possible third period of dissolution and karstification is suggested by the extensive cavity fillings by Pennsylvania fluviatile sediments. Filling of cavities in Davenport-Spring Grove host rocks is virtually complete (this includes cavities over 10,000 cubic meters in volume). The majority of cavities in Cedar Rapids host rocks are also filled. The presence of green shale clasts in Pennsylvania mudstone indicates the dislocation of earlier fill, perhaps through enlargement of pre-existing green shale-filled openings, or downward movement of green shale from higher openings.

The earliest epigenetic mineral precipitated at Linwood was pre-Pennsylvanian calcite. Its time of formation relative to the green shale and Pennsylvania sediment fills is clearly established at least one locality on the Cedar Rapids level. Here, a high angle fracture-controlled cavity floored with green shale was lined with pre-Pennsylvanian calcite. The cavity was subsequently filled with Pennsylvania sediment (figure 7). This generation of calcite precipitation closed many small fractures, particularly in the middle unit of the Cedar Rapids Member, to later fluid migration and mineralization.

Disseminated and concretionary iron sulfide minerals may have precipitated during early stages of diagenesis of the organic-rich mudstones of the sediment fills. Iron sulfides of this type are common in karst-filling mudstones elsewhere in eastern Iowa (Garvin et al., 1987; Garvin and Ludvigson, 1993). The cavity-lining stage of mineralization began with precipitation of marcasite, pyrite and microcrystalline FeS2, which occur as coatings, dustings, encrustations on, and replacement of, carbonate wall-rock. Pyrite appears to precede marcasite, though there is an overlap in their depositional periods. After the precipitation of early pyrite, and before the precipitation of calcite and some of the marcasite, pyrite crusts were dissolved from some cavity walls and subsequently cemented with later-forming minerals, particularly anhedral calcite spar. This same phenomenon has been observed in paleokarst-associated deposits elsewhere in eastern Iowa (Garvin, 1984; Garvin et al., 1995).
et al., 1987), and may be related to solution collapse or tectonic events. Precipitation of FeS2 continued intermittently throughout the period of cavity-lining mineralization. Precipitation of marcasite on barite marks the end of cavity-lining mineralization. Determining calcite paragenesis is a difficult task because the same crystal forms appear in more than one generation and because forms in a single generation may change during growth. Change in form is documented by FeS2 dusting on successive growth surfaces. Growth cessation at different times in different cavities resulted in different external forms. Rare acute rhombohedra modified by acute scalenohedron (type I) formed early (figure 25). A second early calcite (type II) consists of acute scalenohedra, which may or may not be modified by obtuse forms (figures 23-24). Locally, these are perched on mud-coated pre-Pennsylvanian calcite (figure 22). The difference in the two generations is easily observed with ultraviolet light, where pre-Pennsylvanian calcite fluoresces white to creamy white and early post-Pennsylvanian calcite fluoresces pink to dull violet. Age relations between type I and type II could not be determined, but both are overgrown by type III calcite, which consists of obtuse scalenohedra, variably modified by acute scalenohedra and obtuse rhombohedra (figure 26). Small type III crystals are perched syntactically upon some type II crystals (figure 27); other type II crystals are completely overgrown (figure 28). The presence of acute scalenohedra, commonly with type III phantoms, identifies another generation of calcite (type IV) (figure 30). These are often doubly-terminated and appear to have grown upon mud floors (figure 31). A late generation of calcite (type V) appears as rare simple rhombohedra, with minor modification by acute scalenohedra. Its exact position in the paragenetic sequence could not be determined with certainty.

Barite appears late in the paragenetic sequence. In individual cavities it is the last mineral to form, with the exception of marcasite, as previously noted. The paragenetic interrelationships of the several habits of barite could not be determined, since they do not occur together in the same cavity.

Spalhierite formed early in the sequence. It was observed upon thin crusts of marcasite and beneath calcite at several locations. Type III calcite rests on spalhierite at another location.

Summarizing the paragenesis of minerals lining cavities, or in fractures immediately adjacent to them, iron sulfides and spalhierite appear early, calcite follows and barite is late. Iron sulfides continued to be precipitated intermittently during the entire sequence of mineralization. That cavity-lining mineralization occurred after Pennsylvanian sedimentation is evidenced by calcite growths on mudstone (for example, see figure 29).

The paragenesis of minerals wholly within mud fillings parallels that for minerals lining cavities, namely early precipitation of iron sulfide and spalhierite, followed by calcite and barite. A composite paragenetic diagram for all mineralization at Linwood is shown in figure 46.

MINERALIZATION CONTROLS

PHYSICAL CONTROLS

For minerals found in cavities controlled by high-angle fractures, the strike of which could be determined with certainty, an attempt was made to correlate areal distribution of minerals with fracture orientation (Table 1). This tabulation reveals that cavities controlled by northeast-trending fractures are clearly dominant, and that individual mineral distribution broadly parallels that for total minerals. The numbers should be interpreted with caution, since for each mineral there is a substantial number of cavities for which the fracture orientation could not be ascertained.

Vertical distribution of mineralized cavities closely parallels that for total cavities, indicating that mineralizing fluids had more or less uniform access to cavities at all levels (figure 47). The majority of mineralized cavities are bedding-plane controlled and occur in the lowest unit of the Cedar Rapids Member. Distribution of calcite, marcasite and pyrite parallels closely that of total mineralized cavities. Virtually every cavity containing calcite also contains marcasite.

Table 1: Distribution of Linwood minerals in Cedar Rapids -level cavities with respect to fracture orientation.

<table>
<thead>
<tr>
<th>MINERALS</th>
<th>NE</th>
<th>NW</th>
<th>E</th>
<th>N</th>
<th>U</th>
<th>TOTALS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcite</td>
<td>73%</td>
<td>7%</td>
<td>4%</td>
<td>2%</td>
<td>24%</td>
<td>70</td>
</tr>
<tr>
<td>Barite</td>
<td>6%</td>
<td>0%</td>
<td>0%</td>
<td>0%</td>
<td>9%</td>
<td>15</td>
</tr>
<tr>
<td>Pyrite</td>
<td>9%</td>
<td>1%</td>
<td>0%</td>
<td>1%</td>
<td>10%</td>
<td>21</td>
</tr>
<tr>
<td>Marcasite</td>
<td>17%</td>
<td>3%</td>
<td>1%</td>
<td>1%</td>
<td>16%</td>
<td>38</td>
</tr>
<tr>
<td>Total Cavities</td>
<td>75%</td>
<td>26%</td>
<td>17%</td>
<td>11%</td>
<td>50%</td>
<td>179</td>
</tr>
<tr>
<td>Total Mineralized</td>
<td>47%</td>
<td>8%</td>
<td>7%</td>
<td>2%</td>
<td>30%</td>
<td>94</td>
</tr>
</tbody>
</table>

*U = fracture orientation unknown

*33 = number of cavities containing a given mineral which are controlled by fractures of the stated orientation

Figure 40-45. Figure 40. Barite druse (white) on boxwork. Figure 41. Slabs of pyrite overgrown by marcasite. Figure 42. Large pyrite stalactite (center) overgrown by type II calcite. Figure 43. Pyrite stalactites growing from type II calcite crystals. Figure 44. Bladed marcasite on limestone host rock. Figure 45. Etched, subhedral spalhierite (dark) with perched type III calcite (light).
The restriction of multicrystalline (including stalactitic) barite to cavity ceilings and overhanging walls suggests vadose precipitation. Dusting of some barite surfaces by late marcasite indicates a return to phreatic conditions.

The highly-altered nature of some limestone breakdown clasts suggests the presence of low pH fluids. The formation of breakdown is generally regarded as a vadose phenomenon resulting from loss of buoyant roof support due to progressive lowering of the water table. Oxidation of iron sulfide, which is abundant in clast void-filling Pennsylvanian mudstone and green shale, could have provided a source for acid.

The close spatial association between mineral sulfides and organic-rich mudstone suggests a genetic relationship. Carbonate rocks in the ceilings and hanging walls above cavities filled with Pennsylvanian sediment frequently are replaced with iron sulfide and locally with sphalerite, most notably where the uppermost fill is organic-rich mudstone. At one locality on the Cedar Rapids level, an elliptical tube nearly 2 m across is completely filled with sediment consisting primarily of sandstone containing small limestone and green shale clasts. The upper few centimeters of the fill consists of organic-rich mudstone. At the apex of the cavity is an area of sulfide replacement extending 10-15 cm into the overlying carbonate host rock. Hydrogen sulfide gas, generated by bacterial (or thermal?) decomposition of organic matter in these occurrences may have created an environment favorable to sulfide stability. Reaction of rising sulfide-bearing fluids with supraregional carbonate rock may have caused sulfide precipitation.

**ORIGIN OF BOXWORK**

As described previously, boxwork typically forms in chimneys containing accumulations of highly altered breakdown either on floors or in narrow necks. Close inspection of loose boxwork masses reveals the presence of altered limestone and green clay in sheltered voids. The boxwork appears to have formed as follows. First, highly altered limestone and green clay clasts residing on the floor of the cavity were cemented by anhedral calcite spar under phreatic conditions. Second, a change in the cavity to vadose conditions resulted in the washing out of clast material. Third, phreatic conditions returned and euhedral calcite and marcasite were precipitated on the anhedral calcite cements (figure 32,33,48).

**ORIGIN OF STALACTITES**

Iron sulfide stalactites are exclusively restricted to small cavities (< 0.2 m² cross-sectional area), invariably containing organic-rich mudstone floors and surrounded by hard, dense limestone. They are found most commonly in the middle unit of the Cedar Rapids Member. Stalactites, which are typically solid cylindrical to conical masses 1 to 4 mm across at the base, and generally a centimeter or less in length (figure 11v) at a single locality, stalactites up to 5 cm in length were observed (figure 22 u), project vertically from the

**CHEMICAL CONTROLS**

The majority of cavity-lining minerals at Linwood appear to have precipitated under phreatic conditions, as evidenced by the following:

1) the presence of euhedral calcite crystals on all cavity surfaces and the complete absence of vadose spelean calcite (Jennings, 1985; Ford, 1988). The lack of vadose spelean calcite indicates that vadose seepage was undersaturated with respect to calcite or that vadose waters could not access the cavities after water table lowering. The former condition is suggested by the presence of etched euhedral calcite in some cavities.

2) the presence of widespread cavity-lining sulfide minerals, most notably marcasite. Marcasite precipitation was intermittent throughout the entire history of cavity mineralization.

3) the apparent nucleation and growth of calcite, marcasite and prismatic barite in mud fillings and in altered breakdown.
cavity ceiling and, in many cases, appear to have grown from the point of intersection of three contiguous faces of an obtuse-form calcite crystal. Stalactites are partly overgrown with calcite. The core appears to be microscopic iron sulfide overgrown by cubo-octahedral pyrite crystals that are easily visible with a hand lens. Pyrite is often overgrown with bladed marcasite. Stalagmites were not observed in any cavity.

Stalactitic masses of iron sulfide have been observed elsewhere in the vicinity of the Linwood Mine. At the nearby Lafarge Company quarry, cylindrical masses of finely crystalline iron sulfide up to 0.5 cm in diameter exhibiting radial concentric structure occur as broken fragments in a matrix of Pennsylvanian mudstone. Evidences of paleo-karst are abundant in the rocks exposed in the quarry. At the Midway Quarry at Joslin in Henry County, Illinois, cylindrical masses several centimeters in diameter and up to 25 cm in length were reported to project vertically from large cavities in Silurian dolostone (Steve Barnett, University of Iowa, written communication). In two samples observed by the author, cores of these cylinders consist of fine-grained pyrite exhibiting radial structure, overgrown with macrocrystalline pyrite and marcasite and, commonly, clusters of subhedral sphalerite. Central holes are not evident, and, as at Linwood, stalagmites are apparently absent. To the north of the Linwood Mine in Jackson County, cylindrical stalactitic masses of goethite as much as 20 cm in length have been found as flat along ephemeral stream channels. The goethite exhibits pseudomorphism after both pyrite and marcasite. Unaltered pyrite remains in some cores (Steve Barnett, written communication). Sphalerite and marcasite stalactitic forms as much as 2 cm across, but projecting from cavity floors, have been observed in the upper Mississippi Valley zinc-lead district (Heyl et al., 1959). Stalactitic pyrite and sphalerite have been reported in paleokarst in Proterozoic carbonate rocks at Baffin Island (Olson, 1984) and from several localities in Europe (Samama, 1986).

The origin of pyrite stalactites is problematical because stalactite formation is thought to involve the dripping action of water under subaerial conditions; whereas pyrite formation requires reducing, presumably subaqueous, conditions. Oxygen-poor conditions might be attained through organic matter decomposition and hydrogen sulfide degassing in confined cavities (Samama, 1986). The organic-rich mudstone floors of stalactite-containing cavities at Linwood might have provided a source of reducing gases; the dense limestone surrounding the cavity might have confined them. Partial filling of the cavity by water during stalactite growth might explain the absence of stalagmites. Alternatively, stalactites might be products of subaerious precipitation, by what mechanism is not known. Overgrowths of pyrite and marcasite on stalactitic cores likely were products of subaerious precipitation.

COMPARISONS BETWEEN DEPOSITS AT LINWOOD, OTHER PALEOKARST-ASSOCIATED MINERAL OCCURRENCES IN EASTERN IOWA, AND FORMERLY COMMERCIAL DEPOSITS IN THE UPPER MISSISSIPPI VALLEY ZINC-LEAD DISTRICT

OTHER PALEOKARST-ASSOCIATED OCCURRENCES IN EASTERN IOWA

Paleokarst-associated deposits in eastern Iowa and adjacent Illinois are discussed in recent reports (Spry and Kurz, 1988; Kurz and Spry, 1989; Garvin et al., 1987; Garvin and Ludvigson, 1988; 1993). Deposits have also been studied at the Mosco and Lafarge Company Buffalo quarries in Iowa, and the Joslin and Milan quarries in western Illinois (Garvin, unpub. data). These deposits all have much in common with those at Linwood. The mineralogies are similar; the dominant minerals are marcasite, pyrite and calcite, while barite and sphalerite are subordinate. Chalcopyrite is present in some deposits and not in others. With regard to paragenesis, iron sulfides are early, sphalerite is intermediate, and calcite and barite are late. Calcite phantoms are common at Moscow and Lafarge. Mineralization occurs as disseminations in karst-filling sediment, as cavity linings, break-down coatings and cement, fracture fillings and linings of small vugs that are in spatial proximity to larger cavities. Linwood deposits are distinguished from other paleokarst deposits by the presence of pre-Pennsylvanian calcite, a greater abundance and habit variety of barite, and a greater number of generations of calcite. Further comparisons await fluid inclusion and stable isotope compositional investigations at Linwood.

FORMERLY COMMERCIAL DEPOSITS IN THE UPPER MISSISSIPPI VALLEY ZINC-LEAD DISTRICT

Genetic relationships between minor sulfide-bearing mineral occurrences fringing the upper Mississippi Valley deposits (UMV) has been a subject of considerable interest (Heyl, 1968; Heyl and West, 1982; Garvin, 1982; 1984; Ludvigson et al., 1983; Ludvigson and Millen, 1988; Coveney and Goebel, 1983; Coveney et al., 1987; Kurtz, 1987; Spry and Kurz, 1988; Kurtz and Spry, 1989; Garvin et al., 1987; Garvin and Ludvigson, 1988; 1993). On the basis of mineralogy, paragenesis, fluid inclusion temperatures and compositions, and sulfur, carbon and oxygen isotopic compositions, it has been determined that some fringing deposits are similar to some UMV deposits (i.e. pitch-flat deposits), while others are different. UMV and similar-appearing fringing deposits may have formed from the same fluids; fringing deposits which show marked differences in physical and chemical character from UMV deposits are probably not cogenetic. Wide variations in sulfur isotopic compositions among, and even within, some of these fringing deposits, suggest either that fluids were of local diagenetic origin, or that regionally-derived fluids were modified by local fluid-rock interaction (Kurtz and Spry, 1989; Garvin et al., 1987; Garvin and Ludvigson, 1993).

While fluid inclusion and stable isotopic data currently are lacking for the Linwood deposits, comparisons can be made on the basis of mineralogy and paragenesis. All major minerals present in UMV deposits, with the exception of galena, are present at Linwood. Crystallization in open cavities occurs in both deposits, though paleo-karst is rare in UMV deposits and does not occur in rocks hosting the main ore bodies (Heyl, 1983; Heyl et al., 1959). Major mineralogical similarities and differences between the deposits of the two areas are summarized in Table 2.

The paragenetic sequences of Linwood and UMV deposits are similar in that iron sulfides are early, sphalerite is intermediate and calcite and barite are late. In both deposits calcite precipitated in several stages (Heyl et al., 1959). Calcite types between the two areas of mineralization are compared in Table 3. Possible correspondence exists between types I, II, III, and Linwood type V and UMV type IV. Linwood type IV has not been reported from UMV deposits. The above comparisons should be viewed with reserve. It is clear that during the history of calcite precipitation at both localities crystal growth alternated between acute and obtuse types. At Linwood the alternation was at least in some cases gradational, as evidenced by internal zoning. Thus, establishing definitive age relationships is difficult. Without comparative geochemical and isotopic data, meaningful correlations cannot be made with certainty. Microstratigraphic studies of calcites at Linwood may help to define more accurately their age relationships, which in turn may enable more meaningful comparisons with UMV calcites.

SUMMARY AND CONCLUSIONS

Following the deposition of Middle Devonian (Givetian) carbonate rocks, and prior to Pennsylvanian time, extensive karstification...
occurred in eastern Iowa. At the Linwood Mine dissolution of carbonates was most extensive in the Davenport-Spring Grove and Otis limestones. Dissolving waters followed paths controlled by high-angle fractures and horizontal bedding planes and stylolitic partings. Areal distribution of large caverns does not exhibit well-defined patterns, though there does appear to be a preference for northeast-trending fractures on both levels of the mine. On the Cedar Rapids level the majority of cavities are located in the well-bedded lowest unit of the Cedar Rapids Member and they are clearly controlled by horizontal partings. Morphological characteristics of caverns provide evidence that dissolution took place under both vadose and phreatic conditions. Spatial distribution of paleokarst-filling materials provides evidence for multiple dissolution events. Differences in degree of chemical alteration of limestone breakdown, ranging from little or no visible alteration to virtually complete disintegration, indicate significant differences in fluid composition and/or accessibility of fluids to individual cavities.

Cavity-lining mineralization at Linwood is confined chiefly to the Cedar Rapids level of the mine. The distribution of calcite euhedra on all cavity and associated breakdown surfaces, the presence of iron sulfides throughout the entire period of mineralization and the complete absence of vadose spelean calcite indicate that calcite deposition occurred under phreatic conditions. Changes in chemistry of calcite-depositing fluids are demonstrated by alternations between acute and obtuse crystal forms and by the presence or absence of microscopic iron sulfide inclusions on interior growth surfaces. Lack of significant oxidation of iron sulfides indicates that reducing conditions have been maintained in cavities since the time of sulfide deposition. Differences in spatial distribution of barite (monocrystalline forms on cavity floors and as breakdown cements, and multicrystalline forms on cavity ceilings and overhanging walls), suggest that barite deposition was both phreatic and vadose.

Table 2. Comparison of Minerals and Mineral Characteristics Between Linwood and UMV Deposits

<table>
<thead>
<tr>
<th>MINERAL CHARACTERISTIC</th>
<th>LINWOOD MINE</th>
<th>UPPER MISSISSIPPI VALLEY DISTRICT (UMV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrite - coatings and replacements of wallrock</td>
<td>Common</td>
<td>Common</td>
</tr>
<tr>
<td>Pyrite - radial attenuated to colloform</td>
<td>Not observed</td>
<td>Common</td>
</tr>
<tr>
<td>Barite - euhedral prisms</td>
<td>Common</td>
<td>Rare</td>
</tr>
<tr>
<td>Barite - plumose</td>
<td>Locally abundant</td>
<td>Not reported</td>
</tr>
<tr>
<td>Sphalerite - colloform, banded</td>
<td>Not observed</td>
<td>Common</td>
</tr>
<tr>
<td>Sphalerite - euhedral</td>
<td>Common</td>
<td>Common</td>
</tr>
<tr>
<td>Galena</td>
<td>Not observed</td>
<td>Common to locally abundant</td>
</tr>
<tr>
<td>Sallacritic sulfides</td>
<td>Observed - rare</td>
<td>Reported - rare</td>
</tr>
<tr>
<td>Calcite - zoned crystals</td>
<td>Abundant</td>
<td>Abundant</td>
</tr>
<tr>
<td>Calcite - marcasite inclusions</td>
<td>Abundant</td>
<td>Abundant</td>
</tr>
<tr>
<td>Calcite - multiple generations</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Dolomite</td>
<td>Rare</td>
<td>Pervasive</td>
</tr>
<tr>
<td>Quartz</td>
<td>Rare</td>
<td>Pervasive</td>
</tr>
<tr>
<td>Boxwork</td>
<td>Abundant</td>
<td>Not reported</td>
</tr>
</tbody>
</table>

Similarities in presence/absence of mineral species, in multiple generations of calcite, and the overall paragenetic sequence suggest that mineral deposits at the Linwood Mine are cogenetic with nearby paleokarst-associated deposits (e.g., at the Moscow and Buffalo (Lafarge quarries). Comparisons of these same characteristics with those of deposits of the formerly commercial Upper Mississippi Valley Zinc-Lead District also provides evidence for cogenetic. Close correspondence between the several generations of calcite in the two areas is especially noteworthy. Knowledge of precise areal and vertical location of individual mineral samples within the mine will permit systematic investigation of the thermal, trace element and stable isotopic character of Linwood deposits. This information will enable us to enlarge the basis for comparison between Linwood and these, and other related, deposits and to identify possible systematic changes in fluids depositing Linwood minerals.

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