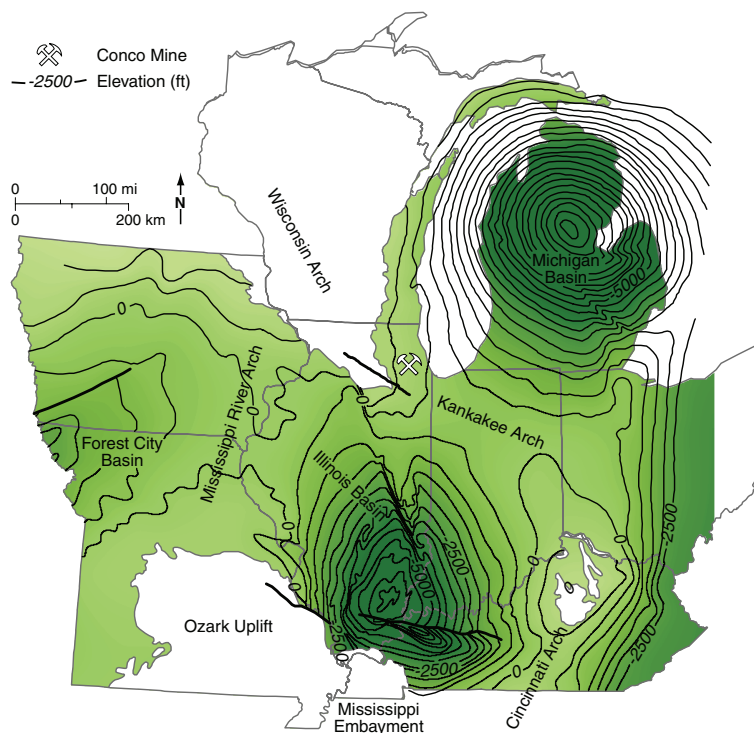


New Insights on Upper Mississippi Valley Mineralization Based on Solution Cavities in the Ordovician Galena Group at the Conco Mine, North Aurora, Illinois, USA

Jared T. Freiburg¹, Bruce W. Fouke², and Zakaria Lasemi¹

¹Illinois State Geological Survey and ²Department of Geology, Institute for Genomic Biology, University of Illinois at Urbana-Champaign



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Front Cover: *Major basins, arches, and domes in the north-central United States in relation to Conco Mine.*

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ABSTRACT

Geologists have long recognized the important role of continental- to basin-scale fluid flow as a mechanism for diagenesis, including the dissolution of rock and the deposition of Mississippi Valley-type (MVT) minerals in sedimentary basins. Tens-of-centimeter- scale calcite crystals, concentrically zoned with sulfide minerals and growing within meter-scale solution cavities, were recently discovered on the flank of the Michigan Basin in the Conco Mine (North Aurora, Kane County, northeastern Illinois). These mineral deposits reflect the temporal changes in chemical composition, fluid flow pathways, and the source of paleofluids migrating through the mid-continent. Meter-scale solution cavities were created by subsurface dissolution along primarily northwest-southeast-trending fractures in the Wise Lake Formation limestone of the Ordovician Galena (Trenton) Group. Plane-light and cathodoluminescent petrography and scanning electron microscopy were used to identify a series of repeating diagenetic events within the cavities: dissolution followed by marcasite, pyrite, and calcite precipitation.

The repetition of these diagenetic events and the paragenetic ordering of mineralization, in conjunction with changes in isotopic ($^{87}\text{Sr}/^{86}\text{Sr}$, $\delta^{13}\text{C}$, and $\delta^{18}\text{O}$) and elemental concentrations (Ca, Na, Sr, Fe, Mg, and Mn) in calcite growth zones, suggest cyclical changes in the fluid chemistry. Furthermore, these repeated changes reflect the source of the subsurface diagenetic waters that were responsible for dissolution and mineralization. The chemical composition of the older, innermost calcite cement zones within the cavity ($^{87}\text{Sr}/^{86}\text{Sr}$, 0.71015 ± 0.00002 standard SRM976; $\delta^{13}\text{C}_{\text{VPDB}}$, -1.62 to -4.88 ; $\delta^{18}\text{O}_{\text{VPDB}}$, -6.99 to -3.37 ; high Mg; and high Fe) is substantially different from the chemical composition of later and younger calcite cements ($^{87}\text{Sr}/^{86}\text{Sr}$, 0.70980 to 0.70898 ± 0.00002 ; $\delta^{13}\text{C}_{\text{VPDB}}$, -3.27 to -10.58 ; $\delta^{18}\text{O}_{\text{VPDB}}$, -8.86 to -6.18 ; low Mg; and low Fe). These differences indicate that there were at least two major events of diagenetic fluids migrating through the country rock.

A comparison of the paragenesis at Conco Mine with that from other regional MVT deposits indicates a related succession of diagenetic events, thus supporting the possible involvement of a similar diagenetic fluid history during dissolution and mineralization. However, the paragenesis at Conco Mine most resembles the paragenesis of the Upper Mississippi Valley Zinc-Lead District deposits, which are thought to be sourced from fluids expelled out of the Illinois Basin. Conversely, the geographic location, structural boundaries, and similar paragenesis of the Conco Mine samples to MVT deposits in the Michigan Basin cannot rule out a Michigan or Appalachian Basin fluid source.

The results of this study have important implications with respect to diagenesis of sedimentary rocks in midcontinent North America, including MVT mineral deposits and factors controlling cavernous porosity development. This study provides documentation and data that help tie the diagenetic features observed in the Galena Group carbonates with potential diagenetic processes, which should help in the development of predictive regional subsurface paleofluid flow models. Enhanced diagenetic and basin flow modeling should improve the accuracy of mineral and hydrocarbon exploration and exploitation models.

INTRODUCTION

The process by which subsurface fluid flow precipitated Mississippi Valley-type (MVT) mineral deposits in sedimentary basins throughout the midcontinent of North America has long been a topic of debate (e.g., Noble 1963, Jackson and Beales 1967, Garven and Freeze 1984, Bethke 1985, Sverjensky 1986, Garven and Raffensperger 1997). Decades of geochemical, geophysical, and hydrological modeling analyses indicate that these mineral deposits precipitated from secondary (diagenetic) formation water during the deep burial water-rock alteration of marine limestone (Hitchon 1984, Oliver 1986, Bethke and Marshak 1990, Garven et al. 1993). However, significant uncertainty remains regarding

the timing, composition, and source of the diagenetic fluids. Therefore, the present study was undertaken to determine whether massively mineralized solution cavities in the Ordovician limestone located in the Conco Mine, North Aurora, Illinois, are the diagenetic result of interaction with (1) MVT hydrothermal waters or (2) more common burial diagenetic waters.

The MVT mineral deposits account for some of the most important reserves and resources of lead and zinc in the world. These epigenetic, strata-bound, carbonate-hosted sulfide bodies are predominately composed of sphalerite, galena, and numerous gangue minerals such as pyrite, marcasite, calcite, and dolomite (Paridas et al. 2007). The MVT deposits are thought to precipitate from deep saline basinal hydrothermal fluids that typically range from 70 to 200°C (Leach and Sangste 1993). The genesis of MVT deposits has been thought to be related to the enhancement of subsurface reservoir rock porosity and permeability, hydrocarbon generation, and subsequent migration (Jackson and Beales 1967, Anderson 1991, Gregg 2004). The economic importance of these enhancements has motivated many previous studies on the nature and genesis of MVT deposits. However, there is still little consensus on interpretation of the genesis, duration, and fluid migration pathways of diagenetic events responsible for MVT mineralization.

This study examines the paragenesis of spectacular mineralization in large solution cavities that have formed within the Ordovician Galena Group in northeastern Illinois. Field relationships have been integrated with high-resolution petrographic and geochemical analyses to reconstruct the timing, composition, and source of the diagenetic fluids from which the minerals precipitated. Furthermore, the paragenetic sequence is compared with other regional MVT deposits as a means of predicting regional subsurface paleofluid flow in order to be able to develop more accurate models for economic mineral and hydrocarbon exploration.

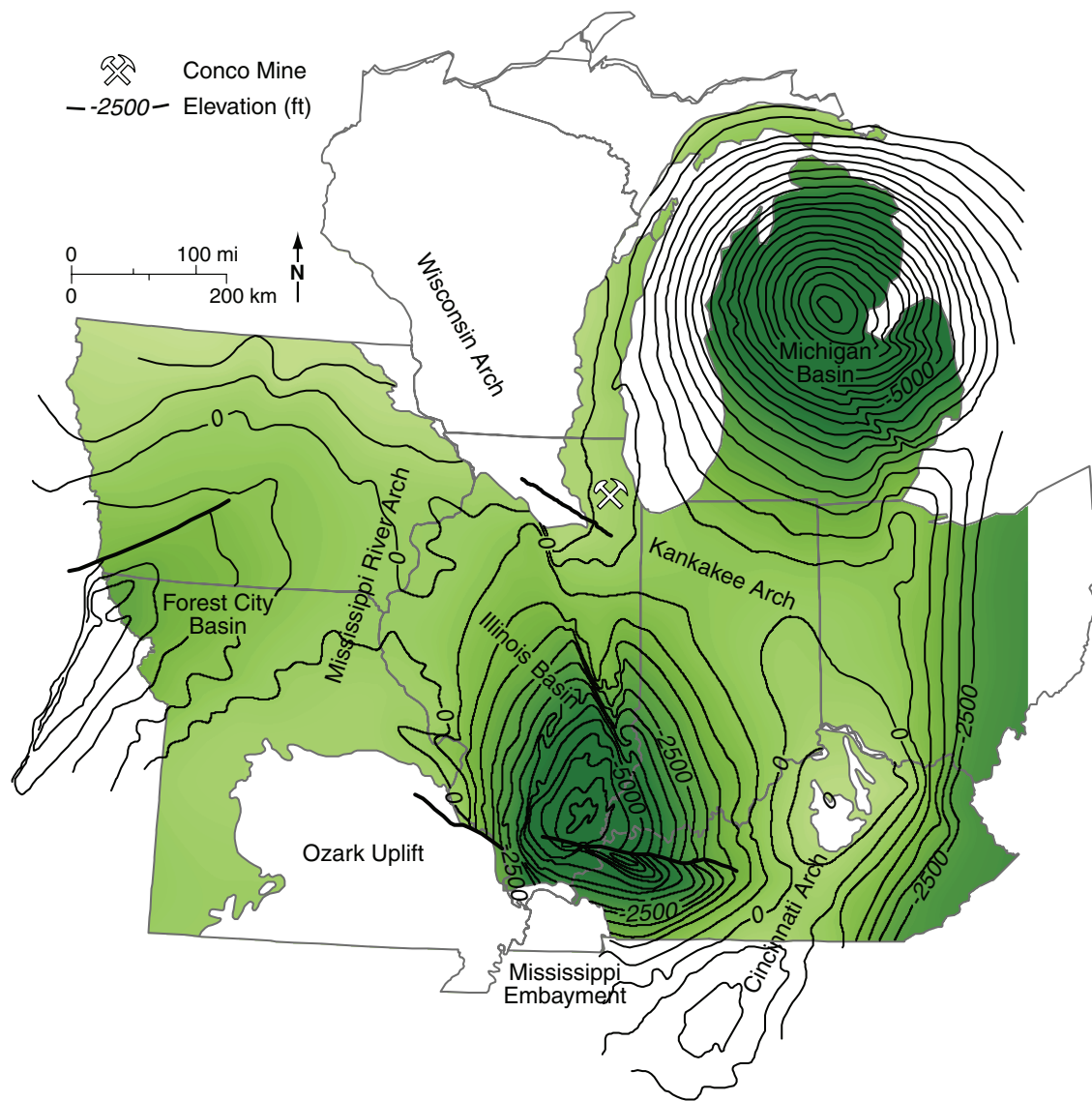


Figure 1 Major basins, arches, and domes in the north-central United States (Cohee et al. 1962, Collinson et al. 1988) in relation to Conco Mine.

Meter-scale solution cavities have been discovered on the southwest flank of the Michigan Basin just off the Kankakee and Wisconsin Arches (Figure 1) in the underground Conco Mine in Kane County, northeastern Illinois (Figure 2). The cavities occur within the late Ordovician carbonates of the Galena Group Wise Lake Formation (Figure 3), which is laterally equivalent to the Trenton Limestone in Michigan, Indiana, Ohio, New York, and Ontario, and the Sinnipee Group in Wisconsin. Calcite cements at tens-of-centimeter scale have pre-

cipitated within the solution cavities that are both obliquely and concentrically zoned with cyclical micron- to centimeter-scale pyrite and marcasite overgrowths. These successive changes in mineral growth zonations are indicative of the changes in bulk subsurface diagenetic fluid properties. The mineralization record within the solution cavities, therefore, directly records the timing and composition of the parent fluids, which in turn provide insight to the source of the diagenetic fluids. These solution cavities and their crystal-

lization sequence, therefore, create a uniquely well-suited natural laboratory in which to study subsurface regional fluid transport, extensive diagenetic alteration, and inference to mechanisms of MVT mineralization.

Late Paleozoic episodes of brine migration in the Illinois, Michigan, and Appalachian Basins originated in the forelands of North American tectonic belts. Migratory pulses of fluid were driven by global-scale tectonic processes (Leach et al. 2001) that resulted in belt deforma-

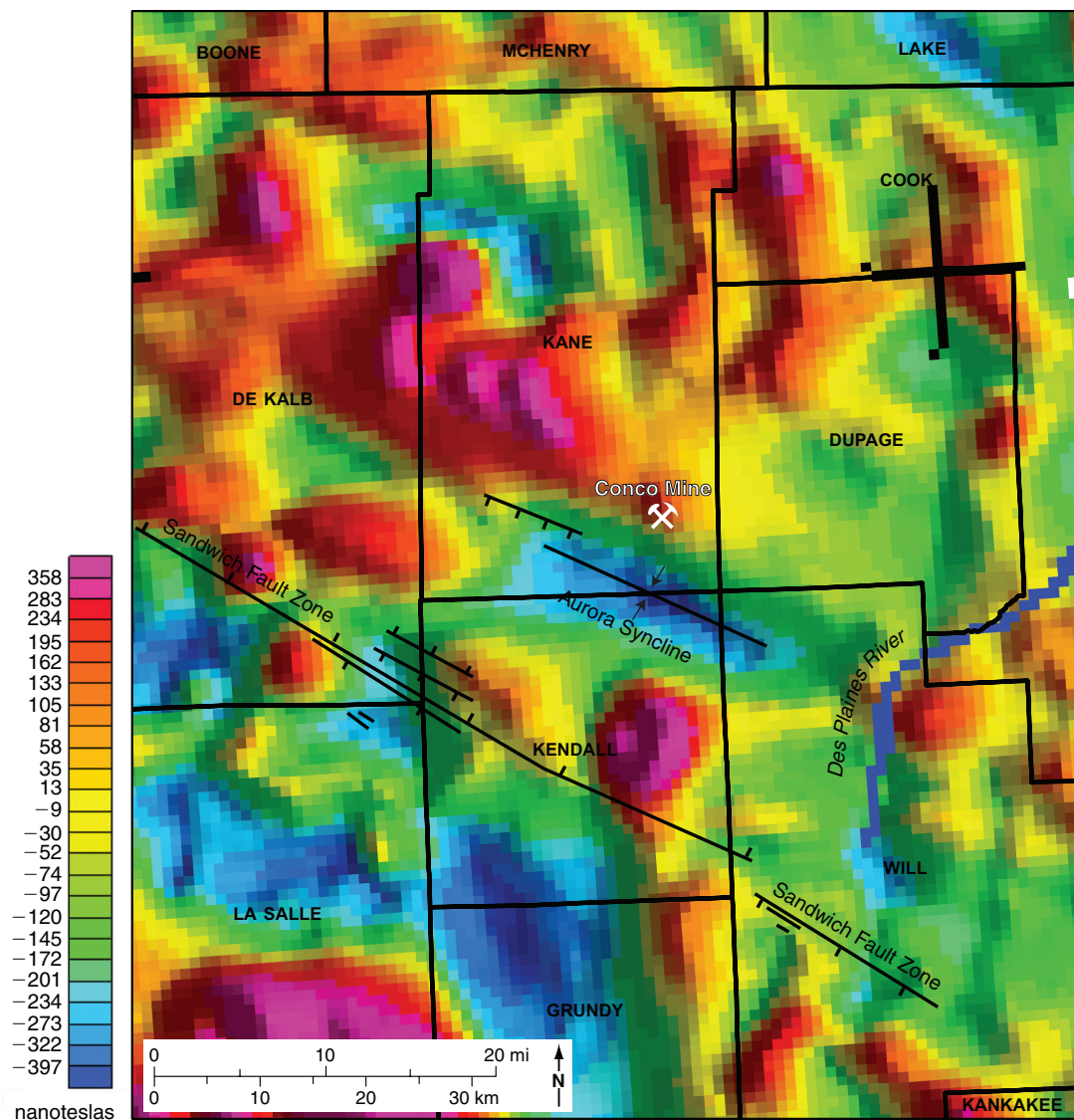


Figure 2 Magnetic anomaly map and structures of northeastern Illinois (Nelson 1995, Daniels et al. 2008). Reds indicate high magnetic pull; blues indicate low magnetic pull.

tion (Bethke and Marshak 1990). This interpretation has been based largely upon early studies of MVT deposits and the relationship of regional or subcontinental-scale hydrologic processes (Jackson and Beales 1967, Sharp 1978, Leach 1979, Anderson and MacQueen 1982, Cathles and Smith 1983, Garven and Freeze 1984, Bethke 1985, Garven 1985, Oliver 1986, Bethke and Marshak 1990, Garven et al. 1993, Garven and Raffensperger 1997, Morrow 1998). The general consensus is that deep basinal brines migrated hundreds of kilometers out of

sedimentary basins before depositing lead- and zinc-rich minerals. Despite this general understanding of the hydrologic processes and recent advances made in dating MVT deposits (Leach et al. 2001), there is still substantial uncertainty about models for ore genesis and the duration, migration pathways, and compositional changes of the depositional fluids at particular deposits (Rowan and Goldhaber 1995).

Many previous studies have given considerable attention to the genesis of lead

and zinc minerals in MVT deposits (e.g., Sverjensky 1986, Garven et al. 1993) due largely to the economic significance of these minerals. However, minerals of little economic importance—commonly referred to as “gangue” minerals such as pyrite, marcasite, and calcite—have rarely been the focus of any study (Brannon et al. 1996, Corbella et al. 2004). The nature of gangue mineralization is significant to tracking the overall depositional fluid evolution and the life span of an MVT deposit. Iron sulfide and calcite mineralization is the main

SYSTEM	SERIES	GROUP	FORMATION THICKNESS (feet)	GRAPHIC COLUMN (not to scale)	DESCRIPTION	
QUATERNARY	HOLO- CENE		Cahokia Fm (0–15)		Alluvium, sand, silt, and clay	
			Grayslake Peat (0–5)		Peat and muck	
			Equality Fm (0–35)		Silt loam, massive	
	PLEISTOCENE	Wedron Fm (0–250)	Henry Fm (0–70)		Sand, silt and clay, laminated	
			Peddicord Tongue (0–35)		Sand and gravel, stratified	
			Robein Silt Fm (0–28)		Till, sand and gravel, laminated sand, silt and clay	
Glasford-Banner Fm (0–375)			Sand, silt and clay, laminated			
Joliet-Kankakee Dol (0–50)			Organic-rich silty clay			
Elmwood Dol (0–50)			Till, sand and gravel, laminated sand, silt and clay			
SILURIAN	ALEXAN- DRIAN		Wilhelmi Fm (0–20)		Dolomite, fine grained	
ORDOVICIAN	CINCINNATIAN	Maquoketa (undiff.)	(0–210)		Dolomite, fine grained, cherty	
			Wise Lake Fm (120–150)		Dolomite; fine grained, argillaceous; shale, dolomitic	
		CHAMPLAINIAN	Galena ("Trenton")	Dygerts		Shale, dolomitic; dolomite, fine to coarse grained, argillaceous
				Dunleith Fm-Guttenberg Dol (35–55)		Dolomitic limestone, fine to medium grained
			Platteville	Quimby's Mill-Nachusa Fm (50)		K-bentonite
	Grand Detour-Mifflin Fm (43)				Dolomite; some limestone, fine to medium grained, cherty, interbedded bentonites	
	Pecatonica Fm (38)			Dolomite, fine to medium grained, with red brown shaly laminae		
	ANCELLIAN	Ancell	Glenwood Fm		Dolomite, fine to medium grained, slightly cherty	
			St. Peter Ss. (60–400)		Dolomite, fine to medium grained, cherty	
	CANAD- IAN	Prairie du Chien (undiff.)	Shakopee Dol		Dolomite, fine to medium grained, cherty, sandy at base	
			New Richmond Ss		Sandstone, poorly sorted; silty dolomite and green shale	
CAMBRIAN	ST. CROIXAN		Oneota Dol (0–400)		Sandstone, white, fine to medium grained, well sorted	
			Eminence Dol (20–150)		Dolomite, fine grained, Dolomite, fine to coarse grained	
			Potosi Dol (90–225)		Dolomite, fine to medium grained, trace sand and glauconite	
			Franconia Fm (75–150)		Dolomite, fine grained, trace sand and glauconite	
			Ironton-Galesville Ss (155–220)		Sandstone, fine grained, glauconitic; green and red shale	
			Eau Claire Fm (350–450)		Sandstone, fine to medium grained, dolomitic	
PRECAMBRIAN			Mt. Simon Ss (1,400–2,600)		Sandstone, fine grained, glauconitic; siltstone, shale, and dolomite	
					Sandstone, white, coarse grained, poorly sorted	
PRECAMBRIAN					Granite, red	

Figure 3 Stratigraphic column of northeastern Illinois (Bauer et al. 1991, Graese 1991). Column is not to scale. Red box indicates rock units encountered at the Conco Mine. Devonian and younger strata were eroded in post-Pennsylvanian times.

emphasis in this study for determining the bulk depositional fluid properties and overall fluid evolution. At MVT deposits, iron abundance in the form of pyrite and marcasite is more variable than Pb/Zn ratios (Leach et al. 1995, Marie et al. 2001, Paradis et al. 2007) and can therefore be used to understand ore genesis. Differences in the fluid property requirements for marcasite and pyrite precipitation create parameters for the fluid flowing through the host rock and fractures. Distinct cyclical zoning of calcite, marcasite, and pyrite cements within the cavities create a temporal sequence relating to the composition and source of the depositional fluids. However, comprehensive analyses of the overall history of deposition and diagenesis (paragenetic sequence) of a particular deposit have rarely been completed (Heyl et al. 1959, Hagni 1986).

In the present study, three-dimensional mapping of field relationships has been combined with detailed plane-light petrography (PL) and cathodoluminescence (CL) analyses, environmental scanning electron microscopy (ESEM), x-ray diffraction (XRD) analysis, elemental abundance, and isotope analyses of the cement stratigraphy within solution cavities. Results have been synthesized to establish a high-resolution paragenetic sequence with which to interpret the depositional and diagenetic history at the Conco Mine in relation to the sequence of mineral deposition within the solution cavities. This paragenetic sequence was then compared with sequences established for MVT deposits and similar studies of MVT mineral-bearing host rock, including (1) the Upper Mississippi Valley Zinc-Lead District (UMV); (2) Ordovician limestone deposited along the eastern Wisconsin Arch in the western Michigan Basin, and (3) Trenton (Galena Group equivalent) hydrocarbon reservoirs in the southern and southeastern Michigan Basin. The high-resolution diagenetic interpretations have been used to reconstruct the timing, composition, and source of the diagenetic fluids responsible for massive dissolution and mineralization of the Ordovician limestone at the Conco Mine.

GEOLOGIC SETTING AND BACKGROUND

To understand the controls on subsurface fluid migration and subsequent rock diagenesis, it is necessary to first review the local and regional geologic setting of the Ordovician limestone at the Conco Mine. Subsurface fluid flow throughout the region is controlled by both structural and sedimentological properties of the regional bedrock (Bethke 1985, Garven et al. 1993, Luczaj 2006). Furthermore, much of the regional subsurface hydrology has been associated with extensive dolomitization of Ordovician limestone, possibly related to carbonate-hosted sulfide mineralization (e.g., Anderson and Macqueen 1982, Gregg 2004, Luczaj 2006). Therefore, the dolomitization history of the Ordovician limestone is also reviewed as an important contextual framework for the present study.

Structural Geology

The research site for this study is located in an underground room-and-pillar limestone mine in North Aurora, Illinois, along the Fox River, approximately 65 km west of downtown Chicago (Figure 1). The mine is located on the continental interior platform known as the midcontinent region of the United States (Sloss 1988, Marshak and Paulsen 1996). The mine lies immediately east of the intersection of the Kankakee and Wisconsin Arches (Pirtle 1932, Ekblaw 1938, Graese 1991). The northwest-trending Kankakee Arch, a southeastern extension of the Wisconsin Arch and Canadian Shield, began development at the close of the Canadian (Early Ordovician) time period, which resulted in the separation of the Michigan Basin to the northeast from the Illinois Basin to the south (Collinson et al. 1988).

In addition to epeirogenic structures such as basins and arches, the region is host to local fold and fault zones that include brittle faults that offset Phanerozoic sedimentary stratigraphic contacts and monoclinial folds that locally tilt the bedding (Marshak and Paulsen 1996) (Figure 2). Two dominant trends of fold

and fault zones throughout the mid-continent are recognized: east-west to northwest-southeast and north-south to northeast-southwest. Regionally and locally, major fault, fracture, and joint systems trend northwest-southeast and northeast-southwest. The Sandwich Fault Zone coincides with the Kankakee Arch and follows this dominant regional northwest-southeast trend (Figure 2). The Sandwich Fault Zone is approximately 135 km long and 1 to 3 km wide (Kolata and Graese 1983). Throughout most of this zone, rock formations are upthrown to the south with a maximum cumulative displacement reaching approximately 245 m in southeastern De Kalb County. However, at the eastern end, in Will County (Figure 2), the fault zone is downthrown to the south with a total displacement of approximately 45 m (Kolata et al. 1978). On the northeast side of the fault zone, Paleozoic strata dip eastward into the Michigan Basin. Conversely, on the southwestern side, the strata dip southward toward the Illinois Basin.

The Conco Mine site is located approximately 35 km northeast of the Sandwich Fault Zone just off the northern flank of the Aurora Syncline (Figure 2). The Aurora Syncline trends eastward across Kane County and then southeastward through Kendall County and into northwestern Will County. The syncline is approximately 3 to 10 km wide and has a maximum relief of approximately 30 m on both contouring surfaces (Nelson 1995). Based on seismic reflection data of poor quality, McGinnis (1966) inferred a large fault just north of the Aurora Syncline trending northwest-southeast through central Kane County. Other studies (Collinson et al. 1988, Heigold 1990, Vaiden et al. 1988) found evidence of smaller faults, but nothing near the magnitude proposed by McGinnis (1966). However, those later studies were mostly localized and may have been areally insufficient to recognize larger, more widespread structural features. A recent magnetic anomaly map of Illinois completed by the U.S. Geological Survey (Daniels et al. 2008) suggests a scissored pattern of magnetic pull trending northwest-southeast. The Aurora Syncline

sits in a magnetic low and is parallel to a magnetic high to the northwest. This magnetic high is followed by a magnetic low to the northwest, similar to the magnetic low of the Aurora Syncline (Figure 2). These magnetic anomalies may reflect deep crustal rock petrology, basement structures such as horst and graben or flower structures, and/or significant deposits of iron sulfides (Sumner 1976).

Regardless, there is evidence for deep-seated structural slip, as suggested by the recent earthquake on February 10, 2010, with an epicenter located just northwest of the Conco Mine at an estimated depth of approximately 5 to 11 km. Within the mine, small vertical faults with centimeter-scale offset are evident, including minor gauge within fractures and trace slickensides along some horizontal clay-rich bedding planes. As previously mentioned, the most prominent features are fractures with no apparent offset but rather host to massive solution cavities. With little to no vertical offset apparent on these fractures, yet with the development of massive solution structures, strike-slip faulting or trans-tensional movement might be suspected (W. John Nelson, personal communication 2011).

Stratigraphy

The midcontinent region of the United States consists of a relatively thin veneer of Phanerozoic strata overlying crystalline basement rock (Sloss 1988, Marshak and Paulsen 1996) (Figure 3). The stratigraphy northeast of the Sandwich Fault Zone, on the southwest margin of the Michigan Basin, consists of Precambrian igneous basement rock unconformably overlain by a sequence of Cambrian to Silurian sedimentary deposits composed of sandstone, limestone, dolomite, and shale. Devonian and younger strata covered the area but were eroded post-Pennsylvanian times (Kolata et al. 1978). Quaternary age glacial drift directly overlies the Silurian bedrock (Figure 3) and generally ranges from 15 to 90 m thick (Kempton et al. 1985); at the mine, however, drift thickness is less than 15 m. This thickness difference is occasionally the case in river valleys where bedrock is typically

exposed. The mine is currently operating in the Wise Lake and Dunleith Formations of the Ordovician Galena Group (Figure 3). The distribution of the Galena Group in northern Illinois reflects the truncation of the southeast-projecting Wisconsin Arch (Willman and Kolata 1978) and the uplift of the Kankakee Arch. The Galena Group comprises a nearly continuous succession (Tippecanoe sequence) of carbonate rocks (dolomite and limestone) deposited on a platform in northeastern Illinois. Galena Group rocks in northern Illinois are dominated by lime mudstone and wackestone interbedded with thin beds of grainstone and packstone and primarily represent a warm, shallow marine environment characterized by low depositional energy (Willman and Kolata 1978). Conversely, rocks of the Galena Group in southern Illinois are dominated by grainstones and packstones that are rich in bryozoans, brachiopods, and echinoderms, suggesting deposition in zones of mixing where cool, nutrient-rich waters encountered warmer shelf waters (Kolata et al. 2001). It has been suggested that North America remained mainly in low latitudes during continental migration during the Paleozoic, thus favoring the deposition of the vast carbonate platforms (Leach et al. 2001) found throughout the midcontinent rock record.

During the deposition of the Ordovician carbonates, a convergent plate boundary developed along the eastern coast of proto-North America, forming continent-wide volcanoes situated in an island arc system (Kolata et al. 1986). The volcanoes deposited widespread ash beds throughout the midcontinent and intermittently throughout deposition of the Galena Group. Over time, diagenetic alteration of the ash beds formed k-bentonite beds (Kolata et al. 1996) or illite-smectite clay-rich beds. Locally, bentonite is encountered in the Wise Lake and Dunleith Formations (Figure 3).

The Galena Group unconformably overlies the Platteville Group (Kolata et al. 1998), which comprises mostly dolomite and cherty dolomite. The Galena and Platteville Groups unconformably overlie the Ordovician Glenwood Formation, a shaly dolomitic sandstone, and the St.

Peter Sandstone, a significant regional aquifer (Figure 3). The St. Peter represents a probable pathway for regional fluid flow and may have played an important role in the transport of diagenetic fluids and the development of solution structures and massive mineral deposits at the Conco Mine.

In northeastern Illinois, the Galena Group is overlain by the Maquoketa Group, which is primarily composed of a thick shale sequence (Figure 3). Many studies have proposed that the contact between the Maquoketa and the Galena represents a subaerial exposure after the deposition of the Galena (Rooney 1966, Taylor and Sibley 1986, DeHaas and Jones 1988). However, more recent studies have concluded that the contact is a submarine hardground (Keith and Wilson 1985, Keith and Wickstrom 1993, Yoo et al. 2000, Kolata et al. 2001). The lowermost formation of the Maquoketa Group is the Scales Shale. The Scales Shale is a mostly dark gray to dark brown shale that creates an excellent impermeable seal over the Galena Group. The Galena Group is laterally equivalent to the Trenton Limestone in Michigan, Indiana, Ohio, New York, and Ontario and the Sinnipee Group in Wisconsin.

Dolomitization

Dolomitization of the Galena Group (Trenton Limestone) has been widely studied and commonly related to MVT mineralization in the midcontinent region (e.g., Budai and Wilson 1986, 1991; Haefner et al. 1988; Gregg 2004; Luczaj 2006; Davies and Smith 2006). Regionally, the Galena Group is extensively to completely dolomitized; however, within the Aurora Syncline, limestone facies have remained only partially dolomitized (Graese 1991). Graese (1991) reported that the lack of dolomitization in the Aurora Syncline implies that the syncline was actively down-warped during deposition of the Galena, thus preventing dolomitization through a mixing-zone model. The Dorag model or mixing-zone hypothesis was first proposed as the cause of regional dolomitization along the Wisconsin Arch by Badiozamani (1973). He indicated that (1) all limestone to the east of the Wis-

consin Arch is not dolomitized based on one data point as a constraint and that (2) Dorag dolomitization was focused exclusively along the arch. Badiozamani (1973) concluded that Dorag-style dolomitization resulted from the mixing of seawater and groundwater in the phreatic zone positioned along the arch. Badiozamani (1973) further suggested that multiple generations of dolomite precipitated during multiple episodes of marine transgression and regression during the Middle to Late Ordovician time.

Several studies cited problems with the Dorag model (e.g., Hardie 1987, Land 1998, Melim et al. 2004). Luczaj (2006) noted many problems when comparing attributes of the hypothetical regional distribution of the mixing-zone model with extensive observations made of the actual regional distribution of dolomite in the Sinnippe Group (Galena equivalent) in eastern Wisconsin and north-eastern Illinois. Luczaj (2006) observed that regionally Ordovician limestone is (1) completely dolomitized to the east of the arch, regardless of structural position; (2) partially to completely dolomitized along the arch; and (3) sporadically dolomitized west of the arch. Luczaj (2006) also found that dolomitized limestone extends eastward well into the Michigan Basin. Luczaj (2006) concludes that if there had been an early regional dolomitization event, it has been overprinted by a later dolomite preserving a hydrothermal signature. Based on petrographic, fluid inclusion, and isotopic evidence, Luczaj (2006) suggests that a hydrothermal dolomitizing fluid sourced from the Michigan Basin is genetically related to MVT minerals on the western margin of the Michigan Basin.

Other detailed studies of the Trenton Limestone (Galena) throughout the Michigan Basin have revealed at least three stages of dolomitization (Gregg and Sibley 1983; Budai and Wilson 1986, 1991; Taylor and Sibley 1986; Fara and Keith 1988; Yoo et al. 2000); the first two stages are strongly to completely overprinted by the third stage throughout western Michigan Basin (Luczaj 2006). Yoo et al. (2000) proposed that the first two stages of dolomitization formed by

evolved Middle and Late Ordovician seawater during the deposition of the Maquoketa Group shale. It was further hypothesized that— during compaction of the shale— magnesium- and iron-rich fluid derived from illitization of smectite in the shale (McHarque and Price 1982) was expelled moving laterally along the top of the Galena, forming a ferroan dolomite cap (Taylor and Sibley 1986, Yoo et al. 2000). Throughout most of the Michigan Basin, the Trenton is limestone with a pronounced dolomite cap (Taylor and Sibley 1986, Fisher et al. 1988), further supporting this hypothesis. Graese (1991) suggested that the Galena cap dolomite does not occur in Kane County except in the Aurora Syncline where it overlies a mostly limestone facies. Petrographic, fluid inclusion, and geochemical studies suggest that the third stage of dolomitization was initiated along the margins of the Michigan Basin when hydrothermal, saline fluids emerged from the deeper part of the Michigan Basin (Coniglio et al. 1994, Yoo et al. 2000, Luczaj 2006) or the Appalachian Basin (Haefner et al. 1988).

Deeper in the Michigan Basin, along the southern margin, hydrothermal dolomitization is concentrated along synclinal sags that are famous for cavernous porosity such as the Albion-Scipio and Stoney Point oil fields (Figure 1) (Shaw 1975, Taylor and Sibley 1986, Budai and Wilson 1986, Hurley and Cumella 1987, Hurley and Budros 1991, Davies and Smith 2006). Albion-Scipio and Stoney Point fields are characterized by an en echelon series of faulted and fractured graben structures that trend N30° W; the overall field trends N15° W. Vugs, fractures, and caverns are typically lined with saddle dolomite (Radke and Mathis 1980). Taylor (1982) describes vertical fracture zones at the Albion-Scipio Trend as dolomite dikes (Haefner et al. 1988). Fracture fill dolomites are commonly associated with anhydrite, calcite, pyrite, marcasite and trace amounts of later stage fluorite, sphalerite, and barite (Shaw 1975, Budai and Wilson 1986, Hurley and Budros 1991), suggesting a genetic relationship. It should also be noted that the Galena Group host rock in the UMV district in northwestern Illinois is primarily

dolomitized but becomes less dolomitized or closer to a limestone-dolomite interface west of the Wisconsin Arch (Heyl et al. 1959). Heyl et al. (1959) also notes a regional dolomitization event overprinted by a later-stage ore-related dolomite cement lining fractures, vugs, and cavities.

Studies along the margins of the Michigan Basin (Shaw 1975, Budai and Wilson 1986, Hurley and Budros 1991, Luczaj 2006) and along the northwestern margin of the Illinois Basin at the UMV (Heyl et al. 1959) suggest a paragenetic relationship between a late stage dolomitization event and MVT mineral precipitation events. Furthermore, petrographic, fluid inclusion, and geochemical evidence supports a hydrothermal fluid origin of the late-stage dolomite (Colquhoun 1991, Yoo et al. 2000, Smith 2006) and the MVT minerals (Haefner et al. 1988, Luczaj 2006).

METHODOLOGY

Sampling

This project was undertaken to better understand the hydrologic and diagenetic controls resulting in the formation of massive solution cavities and subsequent mineral precipitation in the upper Ordovician Galena Group in northeastern Illinois. This investigation included a structural, sedimentological, and stratigraphic study with high-resolution petrographic microscopy and geochemical analyses to ultimately compile a detailed paragenetic sequence for the mineralization events that have filled solution cavities within the Conco Mine.

The Conco Mine began as a surface operation extracting Silurian age dolomite (Figure 3). Due to surface permitting constraints and depletion of near-surface reserves, a decision was made to begin subsurface mining operations of the Galena Group dolomitic limestone. The thick overlying Maquoketa Group shale (Figure 3) makes a structurally sound roof and made tunneling or ramping down to the Galena feasible. The mine is divided into two locations based on property ownership: the North Mine (owned by Lafarge) and the South Mine (owned by the City of Aurora). The dimension of the North Mine is approxi-

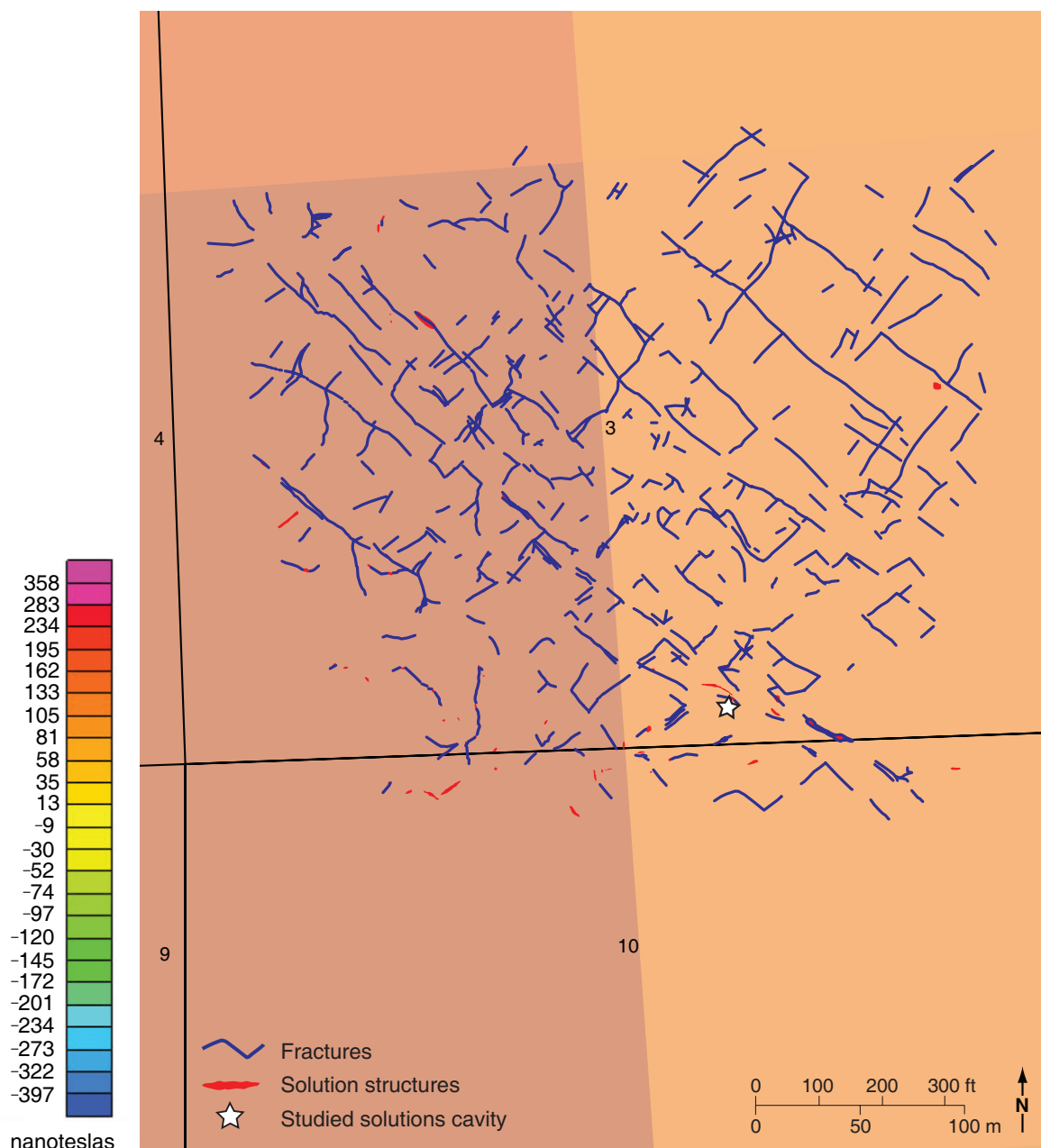


Figure 4 Mapped fractures and solution cavities in the Conco Mine overlying local magnetic anomalies. Subsurface fractures outlined in blue were mapped in the Wise Lake Formation in level 1 of the mine. Solution structures in red primarily coincide with mapped fractures. Note that mapped cavities do not include all cavities as mine personnel have only recently begun to map them. The cavity described in this study occurs on mine level 1. The roof of mine level 1 is approximately 80 m below the surface.

mately 595 m long and 623 m wide, and the South Mine is approximately 736 m long and 427 m wide. Both mines are mined using the room-and-pillar method and have two levels. Each level contains numerous rooms and pillars; each excavated room is approximately

15 m wide and 15 m high with equally measured support pillars. Due to limited access and safety constraints within the mine, only one room in the North Mine was accessible for the current research.

It should be noted that many cavities exist throughout the mine and have only

recently begun to be mapped (Figure 4). Many of the unmapped cavities were blasted out during mining operations. Other cavities that are mapped were not accessible due to mining activities and/or the location of the cavity (above bench levels or near the roof). However,

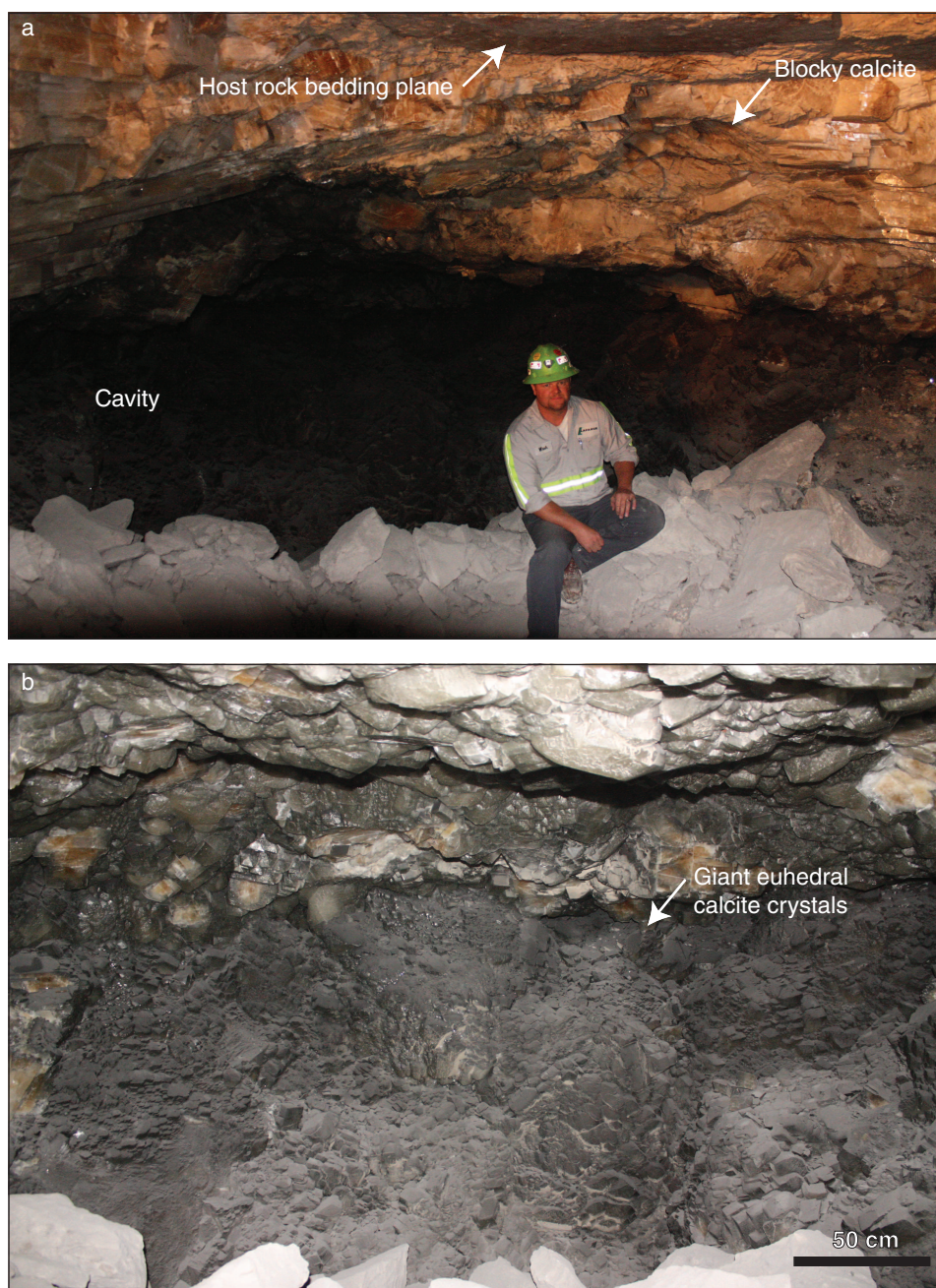


Figure 5 (a) The studied solution cavity showing its elliptical shape (with mine foreman for scale). (b) Giant euhedral calcite crystals line the cavity wall.

during reconnaissance for an accessible and representative cavity to complete this study, observations were made of other cavities visited throughout the mine and are briefly reviewed in the results for reference to the overall paragenesis of the solution cavity formation and mineralization. One cavity exposed within the east pillar on the floor level

of the room was chosen for the research due to its accessibility (Figure 5). Another cavity exposed on the adjacent pillar is described, but the location near the roof of the room made it inaccessible for sampling (Figure 6).

The paragenetic sequence is derived from the synthesis of observations

to create a relative temporal framework from which the depositional and diagenetic history of the rock are reconstructed (Fouke et al. 2005). The paragenetic sequence also provides a framework to help constrain interpretation of the geochemical data. In order to construct a comprehensive paragenetic sequence, it was necessary to

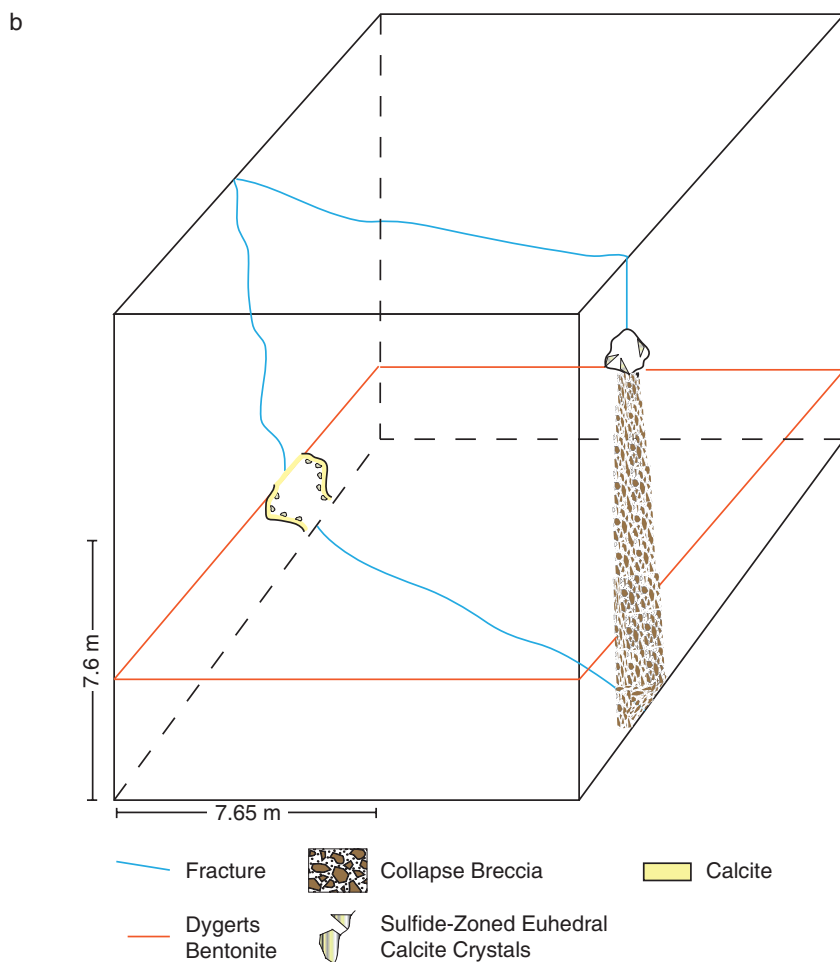
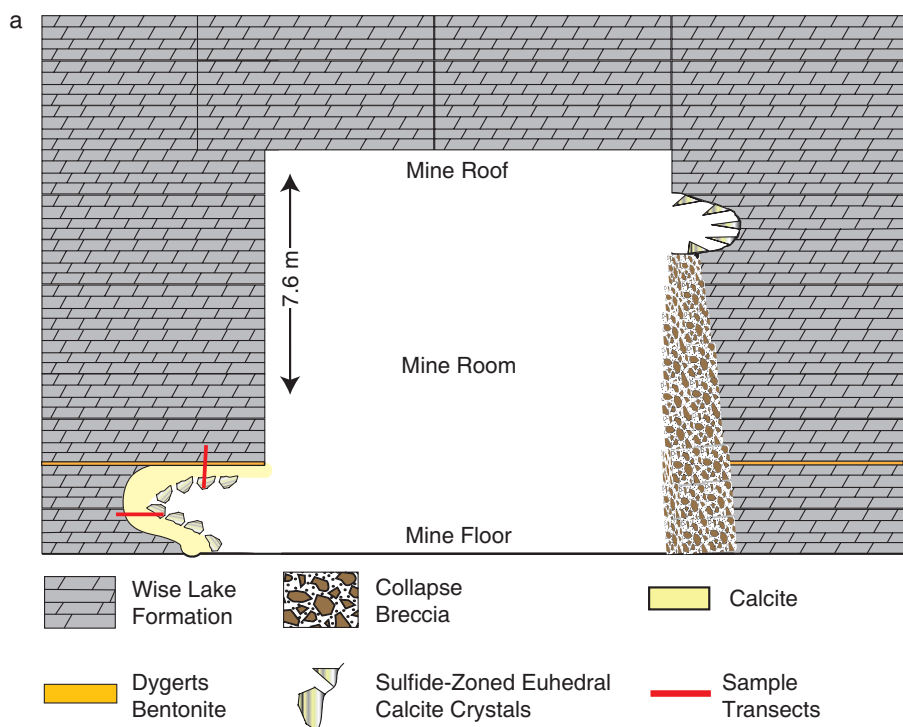


Figure 6 (a) A two-dimensional sketch of the mine room containing the solution cavity (lower left) shown in Figure 5. Samples were taken across vertical and horizontal transects based on field observations. Directly adjacent to the studied cavity is a collapse breccia. Above the breccia is a smaller solution cavity lined with calcite scalenohedrons. Both cavities and the collapse breccia are located along the same northwest-trending fracture. (b) A three-dimensional sketch of the mine room of Figures 5 and 6a. The walls or pillars of the room are composed of the Wise Lake Formation, a dolomitic limestone. The room is approximately 15 m by 15 m. A linear vertical fracture penetrates the roof and down the pillars of the room intersecting the solution structures. These structures include the studied solution cavity located directly below the Dygers bentonite and an adjacent smaller cavity located closer to the roof. Below the smaller cavity is a collapse breccia consisting of large blocks of calcite-spar in a marcasite- and pyrite-rich sucrosic dolomite matrix.

systematically sample the cavity host rock and each of the mineral cements precipitated within the solution cavity. Thus, cements were first mapped within the cavity using physical observations of properties such as color, mineralogy, and cement geometries to differentiate temporal boundaries. Multiple cement generations were recognized based on these observations. Each individual cement generation was sampled accordingly (Figure 7). Ten samples were taken across two linear horizontal and vertical transects (Figure 5). These sampling transects accounted for each cement generation that grew horizontally and vertically within the cavity and also included samples of the host rock above the cavity and horizontally away from the cavity. Each sample was labeled and photographed in place before it was carefully extracted with a hammer and chisel. Each side of the extracted samples was then photographed. Samples were then described before sawing representative samples approximately 25 mm wide, 40 mm long, and 10 mm thick for thin section preparation. Samples were cut using an Edco TMS 10 tile saw. One to two standard, uncovered and

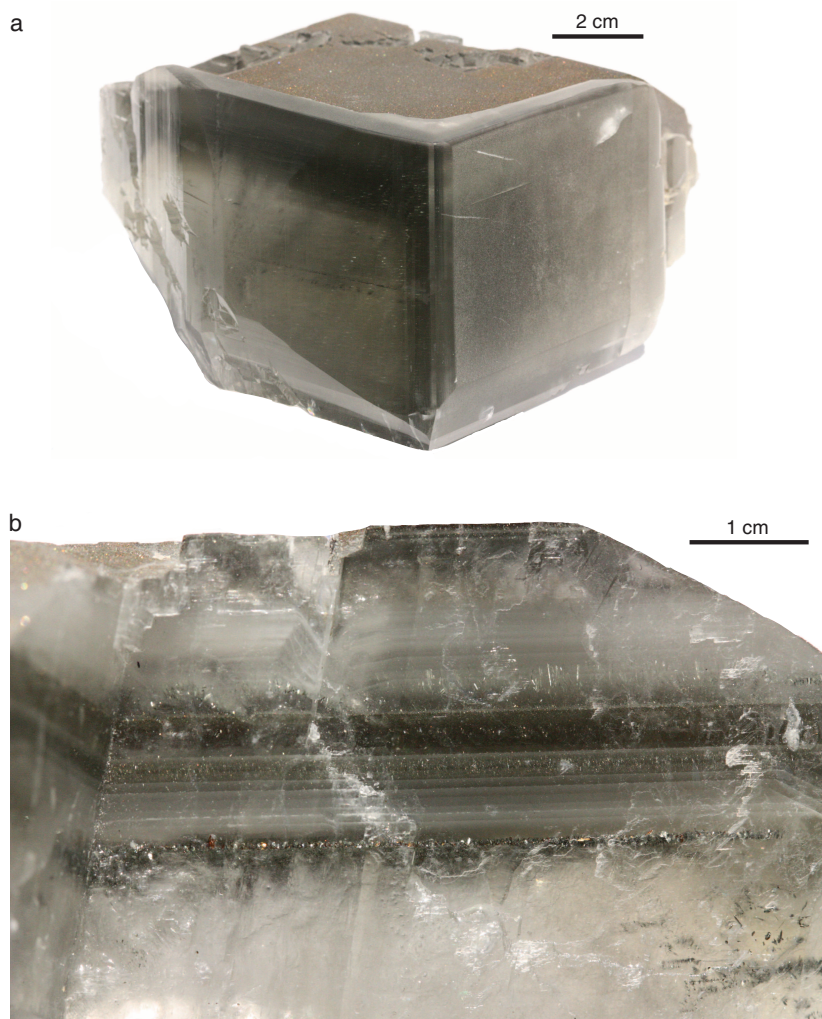


Figure 7 Photographs of a representative euhedral calcite crystal lining the solution cavity wall (Figure 5b). (a) Large calcite crystal from studied cavity. The prominent crystal face is calcite zone C-7 in the paragenetic sequence, and the sulfide zone exposed on top is sulfide zone S-7. (b) Cross section of the same crystal, displaying high-frequency calcite-sulfide zones.

polished thin sections, approximately 30 μm thick, were prepared from each hand sample. Thin sections were impregnated with a clear epoxy. All thin sections were prepared by Wagner Petrographic in Lindon, Utah.

Plane-Light Petrography and Cathodoluminescence

The PL and CL analyses were completed on each thin section to determine the paragenesis of each sample. Polished thin sections were examined using a

CITL cold cathode luminescence 8200 MK3 stage (operating at 12 to 15 kV and 550 μA) at the University of Illinois at Urbana-Champaign. An Optronics DEI-750 three-chip HCCD thermoelectronically cooled camera was used to capture and manipulate the low-light CL images directly (Fouke and Rakovan 2001). Solution cavity limestone host rock was described and classified using the Dunham (1962) classification scheme. High-frequency sulfide and calcite cementation events were paragenetically identified and further described using petrographic, cathodoluminescence,

x-ray diffraction (XRD), and environmental scanning electron microscope (ESEM), mass spectrometer, and electron microprobe analysis.

X-ray Diffraction

Following petrographic description, XRD was used to identify the mineralogy of each sulfide zone. Analysis was completed at the 3M Materials Chemistry Laboratory at the University of Illinois (http://chemistry.illinois.edu/about/facilities/x-ray/introduction_to_service_facility.html). A 100- μm drill bit was used to sample individual sulfide zones embedded in calcite crystals. The XRD data were then collected on a Bruker General Area Detector Diffraction System (GADDS) equipped with a P4 four-circle diffractometer and HiStar multiwire area detector.

Environmental Scanning Electron Microscopy

Based on the XRD results, individual sulfide zones were imaged to determine paragenetic ordering of the minerals and the mineral morphology within each sulfide zone. Back-scattered imaging was completed on an ESEM at the Microscopy Suite at the Beckman Institute, University of Illinois at Urbana-Champaign (<http://itg.beckman.illinois.edu/>). Samples were prepared by breaking calcite crystals along sulfide zones. A few pieces of calcite with each individual and specified sulfide zone were then bathed in a 5.0 pH acetic acid solution buffered with sodium acetate. Samples were monitored every 12 hours in order not to dissolve all calcite and to only partially expose sulfide crystals. Samples were bathed for approximately 60 hours before removal. Samples were then washed with Millipore purified water, dried, and mounted with carbon tape to an ESEM stage plate. Samples were sputter-coated with Au/Pd for approximately 70 seconds. Back-scattered images of sulfide crystals were taken on a Phillips XL30 Field-Emission Environmental Scanning Electron Microscope. Images were compared with petrographic observations and XRD results to determine the mineralogy and paragenesis of each sulfide zone.

Radiogenic Isotope Analyses

Strontium ratios ($^{87}\text{Sr}/^{86}\text{Sr}$) were used to constrain the source of the diagenetic fluids and subsequent water-rock interaction. Analyses of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were completed on the cavity cements and compared with regional formation water to further constrain the source of the diagenetic fluids.

These analyses were completed prior to the beginning of this study and, therefore, are limited to three calcite zones that were sampled prior to the development of the detailed paragenetic sequence. Samples were prepared and run at the University of Illinois at Urbana-Champaign Geology Department, using an NU Plasma HR multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS; <http://www.geology.uiuc.edu/about/ICPMS/index.html>). Three calcite zones were microdrilled using a 100- μm drill bit, and microsampled powders were collected. Approximately 20 mg of powdered sample was weighed and added to 500 μl of 3 *N* nitric acid using a clean pipette. Upon dissolution, the samples were centrifuged for 5 minutes at 300 rpm to separate undissolved, suspended particles from the solution such as sulfide minerals. Then 300-mL samples were loaded into columns containing preconditioned 0.25 strontium-specific resin. One microliter of 3 *M* nitric acid was passed through the column followed by 2 μl of 3 *M* nitric acid added three times. Strontium was then collected by passing 2 mL of 0.05 *M* nitric acid through the columns twice. The solution was then evaporated until it was dry. The dried samples were then dissolved in 2 mL of 2% nitric acid for MC-ICP-MS analysis. Samples were screened for concentration and introduced MC-ICP-MS using a desolvating nebulizer in auto-sampling mode using Ar as the sweep gas. For quality control, duplicates were run on each sample, yielding a precision of approximately $\pm 2\text{E}-05$. The precision of an unprocessed (SRM 979) standard was approximately $\pm 2\text{E}-05$. Also, a processed coral standard was run and was 2.3E-06 lighter than expected ($^{87}\text{Sr}/^{86}\text{Sr}_{\text{coral}} = 0.70919$). Precision of reported results is approximately

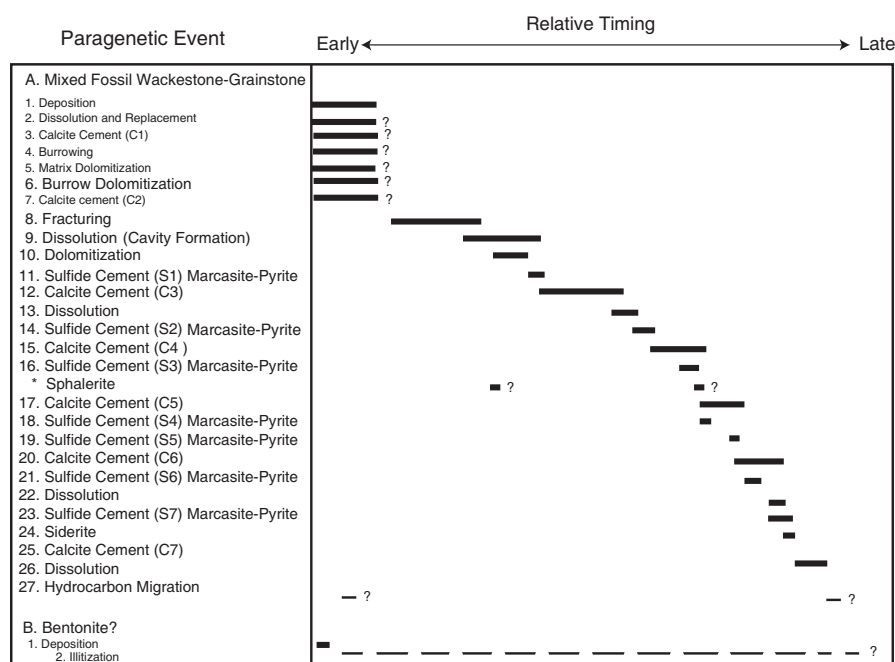


Figure 8 Paragenetic sequence of the solution cavity and the surrounding host rock. The paragenetic events forming the solution cavity and mineralization within are emphasized by larger fonts.

$\pm 2\text{E}-05$. Finally, a blank sample was screened to check for contamination during preparation, and Sr, Rb, Ca, Ba, and Kr concentrations were commensurate with background concentrations.

Stable Isotope Analysis

The $\delta^{13}\text{C}_{\text{VPDB}}$ and $\delta^{18}\text{O}_{\text{VPDB}}$ isotopes are used to further constrain the composition and source of the diagenetic fluid. The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values are reported relative to the Vienna Pee Dee belemnite (VPDB) reference standard as calibrated through analysis of NBS-19 with values of 1.95‰ and -2.2‰, respectively (Coplen et al. 1983). The $\delta^{13}\text{C}_{\text{VPDB}}$ and $\delta^{18}\text{O}_{\text{VPDB}}$ analyses were completed on five calcite cement zones within the solution cavity using three samples from each zone except one zone where four were used. Sample powders were acquired by microdrilling the hand samples described in the preceding sections. Sample powders were analyzed at the Illinois State Geological Survey by the Isotope Geochemistry Section using a Finnigan Mat 252 isotope ratio mass spectrometer with an attached Kiel III Individual Acid Bath Carbonate Device.

Samples were reacted with 100% phosphoric acid at 70°C. Reproducibility for $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ is typically less than $\pm 0.1\text{‰}$ and $\pm 0.15\text{‰}$, respectively. Six standards were run with the sample set, and duplicates were run on one sample.

Elemental Analyses

Electron microprobe analysis (EMPA) was completed at the Electron Microprobe Laboratory, Department of Geology and Geophysics, University of Minnesota, Twin Cities. Elemental abundances were obtained for Ca, Na, Sr, Fe, Mg, and Mn for the cavity calcite cements by EMPA operating at 15 kV and 5 nA with a beam diameter at 40 μm and obtained for Fe, S, Pb, Zn, and Cu for the cavity sulfide cements by EMPA operating at 15 kV and 20 nA with a beam diameter at 5 μm . Estimated precision is expressed as 95% confidence limits and is typically less than 2 wt% for Ca, Mg, 3 wt% for Fe and S, and 4 wt% for Na, Sr, Mn, Pb, Zn, and Cu. Analyses were completed on the same thin sections prepared for petrographic analyses. Analyses were completed on linear transects every 100 μm across the calcite zones

identified by PL and CL petrographic analyses. Three points were analyzed for each sulfide zone. Sulfide zone (S2) A14 was not available for analyses due to loss of sample. Elemental abundances were averaged for each mineral zone. All results were compiled to reconstruct the paragenetic sequence (Figure 8), describe diagenetic cementation events (Table 1), and interpret the results in the context of multiple diagenetic fluids migrating through the host Ordovician limestone.

RESULTS

Sedimentology and Stratigraphy

The Galena Group has regionally been subdivided into three formations, which include (1) the Guttenberg Formation at the base, (2) the Dunleith Formation in the middle, and (3) the Wise Lake Formation at the top (Figure 3). These formations are relatively continuous and uniform in composition throughout northern Illinois (Kolata et al. 2001). Currently, the mining operations at the Conco Mine occur in the Wise Lake Formation. The solution cavity studied is located on the south end of the North Mine, approximately 93 m below ground surface and 28 m below the top of the Wise Lake Formation (Figure 3). Host rock laterally surrounding the cavity is primarily a medium- to coarse-grained wackestone (Figure 9a) with localized thin beds of coarse grainstone (Figure 9b). The grains constituting the wackestone are primarily echinoderm fragments with rare to moderately common skeletal fragments of brachiopods, dasycladacean green algae, pelecypods, and bryozoans (Figure 9a). The matrix also contains trace amounts of fine-grained rounded quartz grains. The grainstone is composed primarily of echinoderm fragments and is typically well cemented with blocky calcite cements (Figure 9b). The host rock just above the cavity is a thin grainstone bed composed primarily of medium- to coarse-grained echinoderm fragments with trace amounts of dasycladacean green algae, pelecypod, brachiopod, and bryozoan fragments cemented by blocky and

syntaxial calcite (Figures 9c, d). Trace amounts of fine, rounded quartz grains are also present. Dolomite is found in the host rock laterally surrounding the cavity and above the cavity. Dolomite in the host rock is primarily a microcrystalline dolomite that has replaced the mud matrix (Figure 10a). In the host rock above the cavity, nonplanar dolomites (Figure 10b) are confined exclusively to slightly branching trace fossil *Chondrites* or *Thalassinoides* burrows (Figure 10c, d). Host rock both above and laterally surrounding the cavity contains trace amounts of planar to subplanar dolomites that are primarily confined to areas of dissolution (Figure 10e). These dolomites are commonly partially dissolved, slightly replaced with sulfide cements, and completely surrounded by calcite cement (Figure 10e). Microfractures cemented with calcite are common throughout the host rock surrounding the cavity (Figure 11a, c).

Directly above the solution cavity, separating cavity cements from the host rock above, is a clay bed (Figure 11b, d). The clay bed lies directly beneath a prominent bedding plane at the base of the host rock above the cavity (Figure 12a, b). Laterally, away from the cavity, the clay bed is difficult to trace but appears to be a consistent bed less than 5 mm thick. Other cavities are observed throughout the mine at the same depth beneath this clay bed (12c, d). The solution cavity and the cavity cements terminate at the base of this clay bed (Figures 11b, d and 13b), and centimeter-scale *Thalassinoides* burrows in the host rock above the cavity terminate at the top of the clay bed (Figure 12b). The clay along this boundary is slightly expanded, especially in the top corner boundaries of the cavity, and contains micrometer- to centimeter-scale pieces of dolomitized host rock (Figures 11b and 12c). The clay is generally a light gray to light blue-green color and exhibits a distinct blue-colored cathodoluminescence (Figure 11b). Fractures where cavities did not develop but that penetrate this clay bed are observed throughout the mine and are commonly filled with an expanded light gray to light blue-green clay.

Structural Geology, Solution Cavities, and Mineralogy

Fractures with consistent northwest-southeast and northeast-southwest orientations were mapped in detail within the Conco Mine by the mine engineer and foreman (Figure 4). Solution structures are exclusively located along fractures; the majority of meter-scale solution cavities are found along northwest-southeast trending fractures. The first occurrence of meter-scale solution structures are found in the first level of the mine, which has a breast back (roof) elevation of approximately 131 m and a bench level (floor) elevation of approximately 116 m. Solution structures have been noted in the roof and all the way down to the floor along fractures. Solution structures have also been found in the second level of the mine but are inaccessible due to mining operations. Two general types of solution structures have been identified throughout the mine: (1) open-spaced cavities and (2) closed-spaced solution structures. This study focuses on the open-spaced cavities and mineralization within those cavities; extensive analyses were completed on a single cavity that was easily accessible. Brief descriptions of other solution cavities and closed-space solution structures throughout the mine are given for diagenetic context to the overall paragenesis at Conco.

The mined-out room chosen for this study contains a prominent northwest-southeast-trending fracture (Figure 4). Along this fracture, in the north pillar of the room, is a highly brecciated limestone (Figure 6), a closed-space solution structure. The breccia is composed of tens of centimeter to centimeter-scale clasts of calcite; centimeter-scale clasts of dolomitized host rock; and marcasite, pyrite, and calcite cements. Miners commonly refer to the breccia as "leopard rock" due to the pattern appearance of iron sulfide precipitated around angular dolomite clasts. The breccia is approximately 2 m thick and appears as a pipe focused along the vertical fracture. Approximately 5 m up along the breccia pipe and near the room roof is a solution cavity lined with euhedral calcite crystals. The cavity is approximately

Table 1 Paragenetic table outlining and describing all diagenetic mineralization events at the Conco Mine.

Paragenetic sequence	Mineralogy	Component	Zone		Color	CL color/ character	Crystal morphology and gross crystal form
			thickness or maximum crystal thickness (cm)	thickness (cm)			
A3 (C1)	Calcite	Microcrystalline-blocky replacement	NA	NA	NA	Light purple to yellow-orange, nonzoned	Microcrystalline
A5	Dolomite	Microcrystalline replacement	<0.001	NA	NA nonzoned	Dark to light purple,	Microcrystalline
A6	Dolomite	Nonplanar cement	0.030	NA	NA	Dark purple, nonzoned	Nonplanar, equant
A7 (C2)	Calcite	Blocky-syntaxial replacement cement	NA	NA	NA	Purple to dark orange, nonzoned	Equant blocky and syntaxial calcite Marcasite: irregular, tabular and prismatic, commonly twinned; pyrite: octahedral and pyritahedral
A11 (S1)	Marcasite-pyrite	Replacement bladed cement	0.030	0.030	Gold-dark brown	NA	Equant blocky calcite Marcasite: Interconnected spear-shaped coating, tabular, and rhombohedral
A12 (C3)	Calcite	Blocky cement	38–102	38–102	Dark yellow to cloudy white	Deep purple	
A14 (S2)	Marcasite-pyrite	Replacement bladed to crystalline cement	0.035	0.035	Brassy gold	NA	
A15 (C4)	Calcite	Blocky cement	10–35	10–35	Dark yellow to cloudy white	Purple to red, gradual	Equant blocky calcite zoning dark to light
A16 (S3)	Marcasite-pyrite	Bladed to crystalline cement	0.040	0.040	Iridescent red-purple-blue-green	NA	Marcasite: radiating blades; pyrite: cuboctahedral
A17 (C5)	Sphalerite	Crystalline	0.500	0.500	Translucent dark brown-purple-red	NA	Highly complex, distorted, and commonly twinned
A18 (S4)	Calcite	Blocky cement	0.050	0.050	Clear	Light purple,	Equant blocky calcite hairline zoning
A19 (S5)	Marcasite-pyrite	Bladed to crystalline cement	0.045	0.045	NA	NA	Marcasite: distorted tabular rhombohedrons; pyrite: distorted stacked octahedrons
A20 (C6)	Calcite	Blocky cement	0.400	0.400	Clear-milky gray	NA	Marcasite: tabular and acicular; pyrite: octahedral and pyritohedral
A21 (S6)	Marcasite-pyrite	Bladed to crystalline cement	0.040	0.040	NA	NA	Equant blocky calcite Marcasite: filamental, acicular; pyrite: cuboctahedral and pyritohedral
A23 (S7)	Marcasite-pyrite	Replacement bladed to crystalline cement	0.050	0.050	Gold-brown	NA	Marcasite: tabular and bladed; pyrite: cuboctahedral, pyritohedral, and cubic
A24	Siderite	Crystalline	0.001	0.001	Yellow-orange	NA	Nonplanar, curved faces, rhombohedral
A25 (C7)	Calcite	Blocky cement	0.5–2	0.5–2	Clear	NA	Rhombohedral (in studied cavity), scalenohedral in other cavities

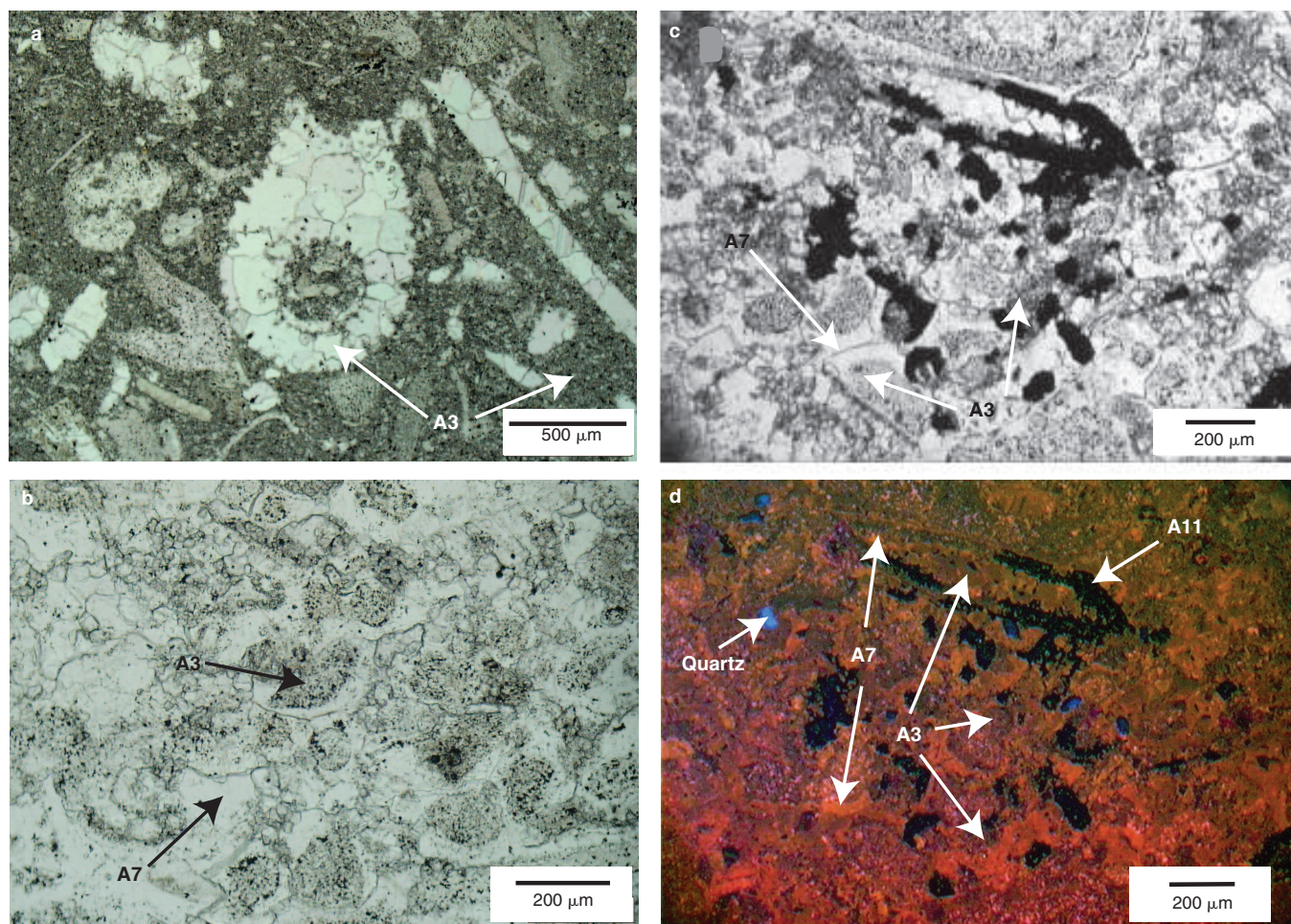


Figure 9 Plane-light petrography (PL) and cathodoluminescent (CL) photomicrographs of solution cavity host rock including paragenetic sequence events (A3, A7, A11). (a) PL photomicrograph of wackestone composed of microcrystalline matrix and medium to coarse grains of echinoderm, green algae, pelecypods, bryozoan, and brachiopod fragments. (b) PL photomicrograph of grainstone composed primarily of echinoderm fragments cemented by blocky and syntaxial cement. (c) PL photomicrograph of grainstone with sulfide cement over earlier blocky and syntaxial calcite cement. (d) CL photomicrograph of previous photomicrograph in c displaying two generations of calcite cement overprinted by later sulfide cement. Trace amounts of rounded quartz grains are also common throughout the host rock.

1 m in width and height and contains primarily tens of centimeter-scale euhedral calcite scalenohedron crystals with micrometer- to millimeter-scale zones of marcasite and pyrite. This cavity was not researched due to its location near the mine roof.

Adjacent to the breccia pipe and smaller cavity and trending along the same fracture is a large solution cavity that is the main focus of this study (Figures 5 and 6a). The cavity descends vertically to an unknown depth. Prior to filling in the cavity for safety reasons, miners

estimated its depth at approximately 30 m. Only the top few meters of the cavity were accessible for this research. The apex of the solution cavity is approximately 1 m above the level 1 floor and opens up in the south pillar or wall of the room (Figure 6a). The top of the cavity has an elliptical shape measuring approximately 3 m × 2 m (Figure 5); however, the original width before excavation was probably more. The cavity walls are completely lined with calcite and sulfide cements (Figures 5 and 7). The calcite crystals are thick, blocky, and often fractured (Figure 5). Euhedral,

intergrown, rhombohedral calcite crystals have grown directly over the blocky calcite cement. A closer examination of all calcite cements precipitated within the cavity revealed calcite growth zones separated by sulfide mineral zones (Figure 7).

To build a contextual framework of the diagenetic events at the Conco Mine, it is necessary to briefly describe the other structures noted throughout the mine. Also, because this is the first extensive study of the solution structures and mineralization at Conco, it is necessary

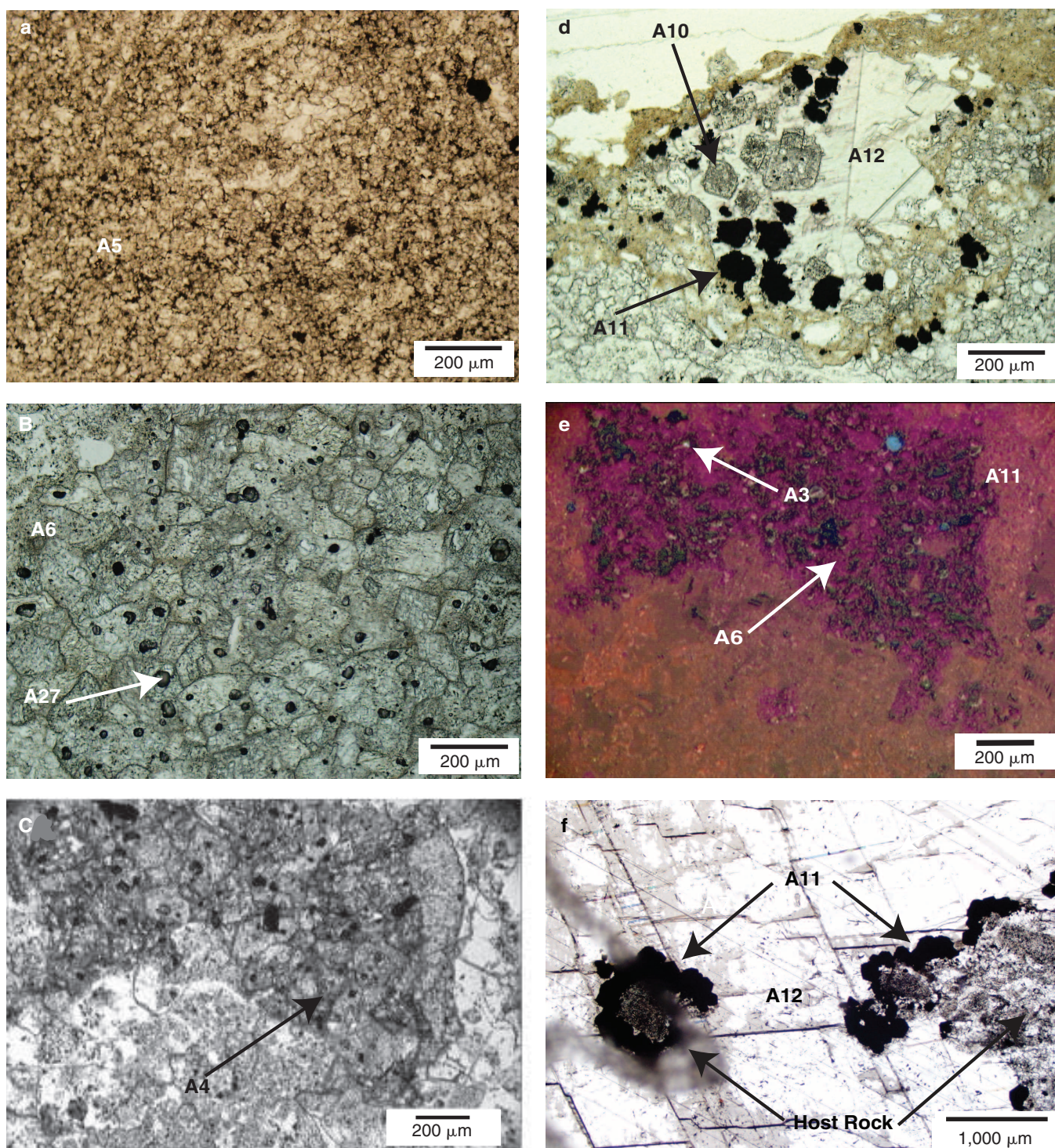


Figure 10 Plane-light petrography (PL) and cathodoluminescent (CL) photomicrographs of rock including paragenetic sequence events (A3, A5, A6, A10, A11, A12, A27). (a) PL photomicrograph of nonplanar microcrystalline dolomite matrix. (b) PL photomicrographs of non-planar dolomites with trace bitumen inclusions infilling burrows (c) in wackestone. (d) CL photomicrograph of burrow dolomites. (e) PL photomicrograph of planar dolomites and sulfide crystals concentrated along dissolution boundary and cemented by blocky calcite. Dolomites are partially dissolved and slightly replaced by a later sulfide cement. (f) "Floating" host rock suspended in the cavity calcite cement C3 and coated with sulfide cement S1.

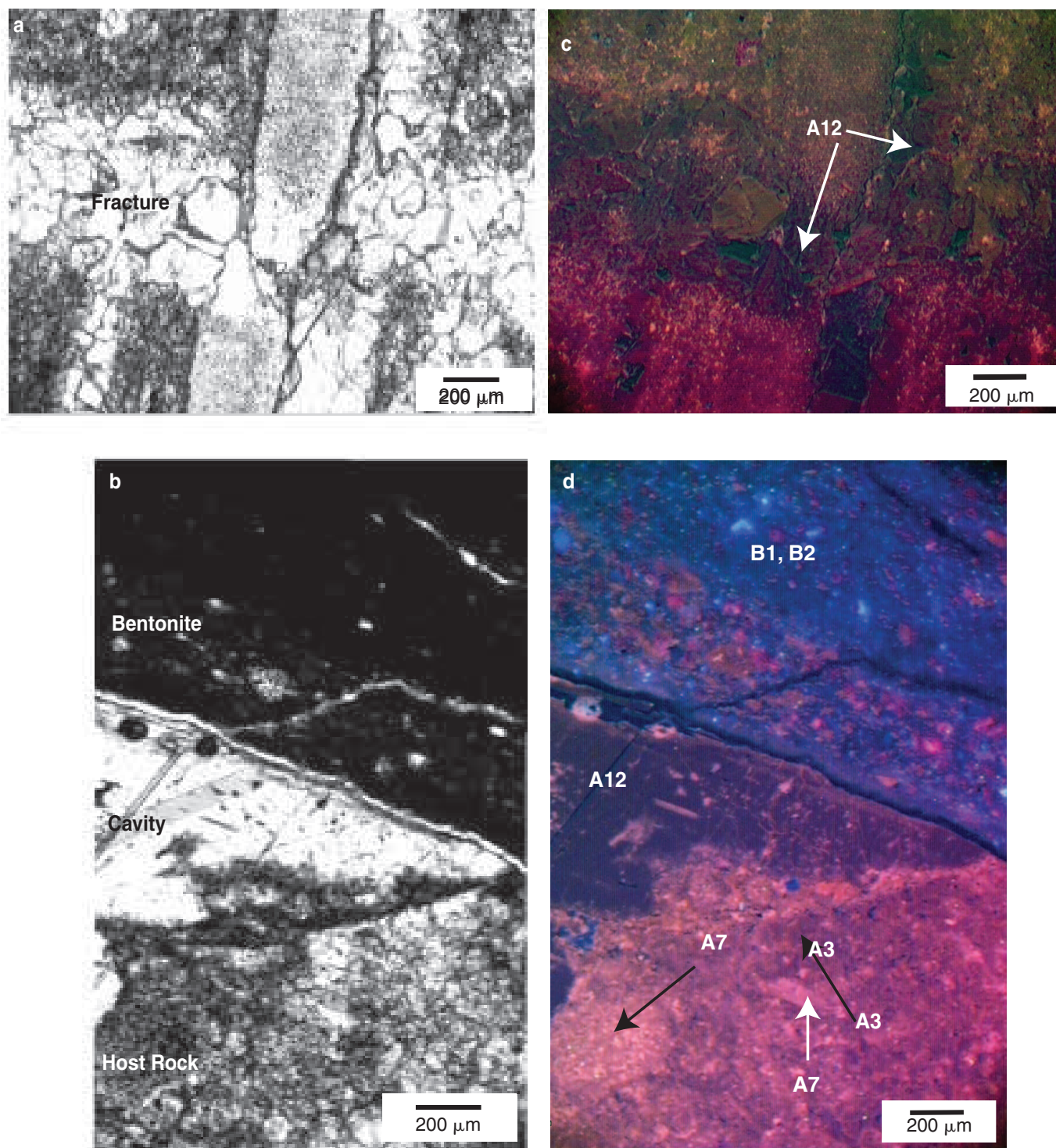


Figure 11 (a) Plane-light petrography (PL) photomicrograph of a fracture crosscutting wackestone and cemented with the first cavity cement (C3) A12. (b) PL photomicrograph of the top edge of the cavity displaying clay bed (Dygers bentonite), cavity calcite cement (C3) A12, and wackestone host rock. (c) Cathodoluminescent (CL) photomicrograph of a fracture crosscutting wackestone and cemented with the first cavity cement (C3) A12. (d) CL photomicrograph of correlating photomicrograph in part b. The clay exhibits distinct blue CL and includes clasts of host rock near its base. The host rock exhibits two distinct calcite generations. Cavity is cemented by first cavity calcite cement (C3) A12.



Figure 12 Photographs of the top east corner of the studied solution cavity (a, b) and another solution cavity within the mine (c, d). (a) Zak Lasemi standing in front of the solution cavity; its top terminates at a prominent bedding plane. (b) Close-up photograph of the same bedding plane shows a slightly swelled Dygerts bentonite with clasts of limestone between the bedding plane and the cavity cements. (c) A different cavity in the north mine shows the cavity (bottom right corner) is focused along a vertical fracture and top of the cavity terminating at the Dygerts bentonite bed. (d) Millimeter-scale Dygerts bentonite bed above cavity.

to briefly describe observed structures and subsequent mineralization for their scientific significance. Brief visits to other open-spaced cavities throughout the mine suggest that the extent of mineralization and crystal growth habits vary within each cavity. The solution cavities that are more laterally extensive than vertically extensive typically are dominated by euhedral calcite crystals growing in a scalenohedral habit (dog-tooth). Single calcite scalenohedrons have been found that are up to 75 cm tall and 25 cm wide. Some scalenohedrons appear to be composed of one single calcite generation varying in characteristics from an extremely high luster calcite to a dull and typically etched calcite.

However, most scalenohedrons include co-genetic and zoned sulfide minerals (pyrite and marcasite) that sometimes exhibit slight iridescent coloring. Scalenohedrons are commonly zoned with sulfide mineralization exhibiting each calcite generation accentuated by sulfide overgrowth. Early generations of calcite growth within the scalenohedron commonly exhibit rhombohedral growth habits overlain by a later scalenohedral calcite growth habit. Calcite and sulfide mineralization is sometimes concentrated around preferentially dolomitized cylindrical burrows. This phenomenon will be documented and discussed in a future publication. The host rock on which the crystals are pre-

cipitated is typically highly dolomitized. Dolomitic host rock is sometimes highly cemented with calcite and other times is poorly cemented to completely unconsolidated and appears as a sucrosic dolomitic sand. Miners commonly refer to it as “sugar” when encountered. Old-time drillers drilling oil and gas wells in the late 1800s in the Giant Lima Trenton Field in eastern Indiana and western Ohio referred to this type of dolomite as “sugar sand”. It was considered one of the best reservoir facies in the Lima Trenton Field (Dennis Prezbindowski, personal communication 2011). Dolomitization is concentrated along the vertical fractures leading to the solution cavities, and dolomitization appears to

be less above the cavity. The majority of fractures, if not all, especially in the south mine, have similar dolomitization concentrated along fractures, even where solution cavities did not develop.

The cavities that are more vertically extensive contain more massive blocky calcite with intergrown rhombohedrons and modified rhombohedron-scalenohedron combination euhedral crystals. Euhedral calcite rhombohedrons and modified rhombohedron-scalenohedron combinations are typically deposited over blocky calcite cement up to 1 m thick and less commonly growing directly on the host rock, unlike the scalenohedron dominant cavities. Single rhombohedron and combined rhombohedron-scalenohedron crystals have been found up to 90 cm in length. Massive sulfide deposits are also found in solution cavities. These include tens-of-centimeter-scale marcasite and pyrite clusters and are typically deposited directly on the cavities' host rock. Most notable are iridescent marcasite and pyrite stalactites growing in large finger-like clusters. Single stalactites have been found that are up to 12 cm long and 4 cm wide. Rarely, a few stalactites have a small inner core. Most stalactites have a structure radiating from the center of the stalactite, which is a common growth habit of marcasite. Green, teal, purple, blue, and silver-black marcasite is found in millimeter-scale bars and centimeter- to tens-of-centimeter-scale colloform masses precipitated on dolomite matrix. Pyrite is rarer and is sometimes found in centimeter-scale clusters of distorted cubes and other times as millimeter-scale octahedrons with a thin copper-red patina coating that appears to be a result of oxidation. However, this coating has not been analyzed. One previous cavity encountered by the miners was nearly barren of mineralization except for a few specimens of massive colloform iron-sulfides, a thin coating of millimeter-scale "ruby jack" sphalerite crystals, and partially dissolved or "skeletal" calcite scalenohedrons zoned with sulfides and up to 6 cm in length. A specimen was recently obtained from this cavity confirming the mineralogy. One other specimen owned by a miner was identified as sphalerite.

Sphalerite crystals are highly complex, distorted, and commonly twinned. Sphalerite crystals have been noted up to 7 mm in size.

Other closed-space solution structures found throughout the mine include dolomitized fractures or pipes. These are solution-enhanced fractures where preferential dolomitization along the fracture occurs up to 2 m laterally away from the fracture, giving the appearance of a pipe. Dolomite is a fine- to medium-grained crystalline sucrosic dolomite that is typically poorly cemented; however, some areas appear to be well cemented by calcite and sulfide minerals. These dolomite "pipes" are commonly highly oxidized, and miners have reported that they occasionally leak fluids. Occasional open-spaced meter-scale cavities occur at top of these pipes, much like the breccia pipe and the small solution cavity adjacent to the studied solution cavity (Figure 6). In the South Mine, fractures with preferential dolomitization are common with trace to no calcite or sulfide cements.

Paragenetic Sequence

A high-resolution paragenetic sequence of the solution cavity and surrounding host rock was reconstructed (Figure 8). The paragenetic sequence reflects a temporal framework of the diagenetic history of the solution cavity studied. Twenty-nine paragenetic events, including deposition and subsequent diagenesis, have been identified. One mineral event is pending. Sphalerite has yet to be identified in place and has not been found in the studied cavity. However, sphalerite has been found in other cavities, and its paragenetic placement in context to the studied cavity is inferred by multiple calcite and sulfide zones found in situ with the sphalerite. The solution cavity mineralization events constituting the bulk of the paragenetic sequence are outlined and described in Table 1. The stratigraphic distribution of each paragenetic event with respect to the solution cavity is used to establish the relative timing of diagenesis.

The host rock surrounding the cavity was deposited primarily as a wackestone

(Figure 9a), including deposition of localized thin beds of fossiliferous grainstone (Figure 9b). A clay zone described as altered bentonite was deposited following deposition of the host rock laterally surrounding the cavity, with subsequent grainstone-wackestone deposition. All wackestone comprises a mud matrix containing echinoderms, green algae, bryozoans, brachiopods, and pelecypods (Figure 9a). Following deposition, dasycladacean green algae and pelecypods internal structures were partially dissolved (A2) and later cemented by calcite (C1) A3 (Figure 9a). The wackestone mud matrix was also partially cemented by microcrystalline calcite (C1) A3 undifferentiated from calcite internally cementing fossils (Figure 9c, d). Most of the echinoderm, brachiopod, and bryozoan fragments retain some original skeletal structures that are also altered to microcrystalline neomorphic calcite (C1) A3 as suggested by CL (Figures 9c, d). Fossils are later cemented with blocky and syntaxial calcite cement (C2) A7 (Figures 9b, c, d). A7 (C2) exhibits brighter CL than A3 (C1) and is typically overprinted with sulfide cement (S1) A12 (Figure 9d).

Some intervals of the host rock wackestone mud matrix are partially to completely replaced by microcrystalline dolomite (A5, Figure 10a). Burrowing of host rock (A4) above the clay bed and likely below occurred following the deposition of the host rock. Non-planar dolomites (A6, Figure 10b) occur exclusively in burrows (Figure 10c). Burrows do not appear to crosscut fossils or calcite cement A3 (C1) and A7 (C3) but exhibit a darker, less intense CL emission relative to the surrounding calcite cements (A3 and A7, Figure 10d). Hydrocarbon (A27) inclusions are found exclusively in burrow dolomites (A6, Figure 10b). However, hydrocarbon coating of mineralized vugs is noted in the top 1.5 m of the Wise Lake Formation in a drill core examined from the South Mine. Fractures (A8, Figure 12a) crosscut host rock, including calcite cement (C1 and C2) A3. Dissolution (A9) is primarily focused along fractures (Figure 11a), but also occurs within some areas of unfractured host rock (Figure 10e). Planar and subplanar dolomites A10 are typically

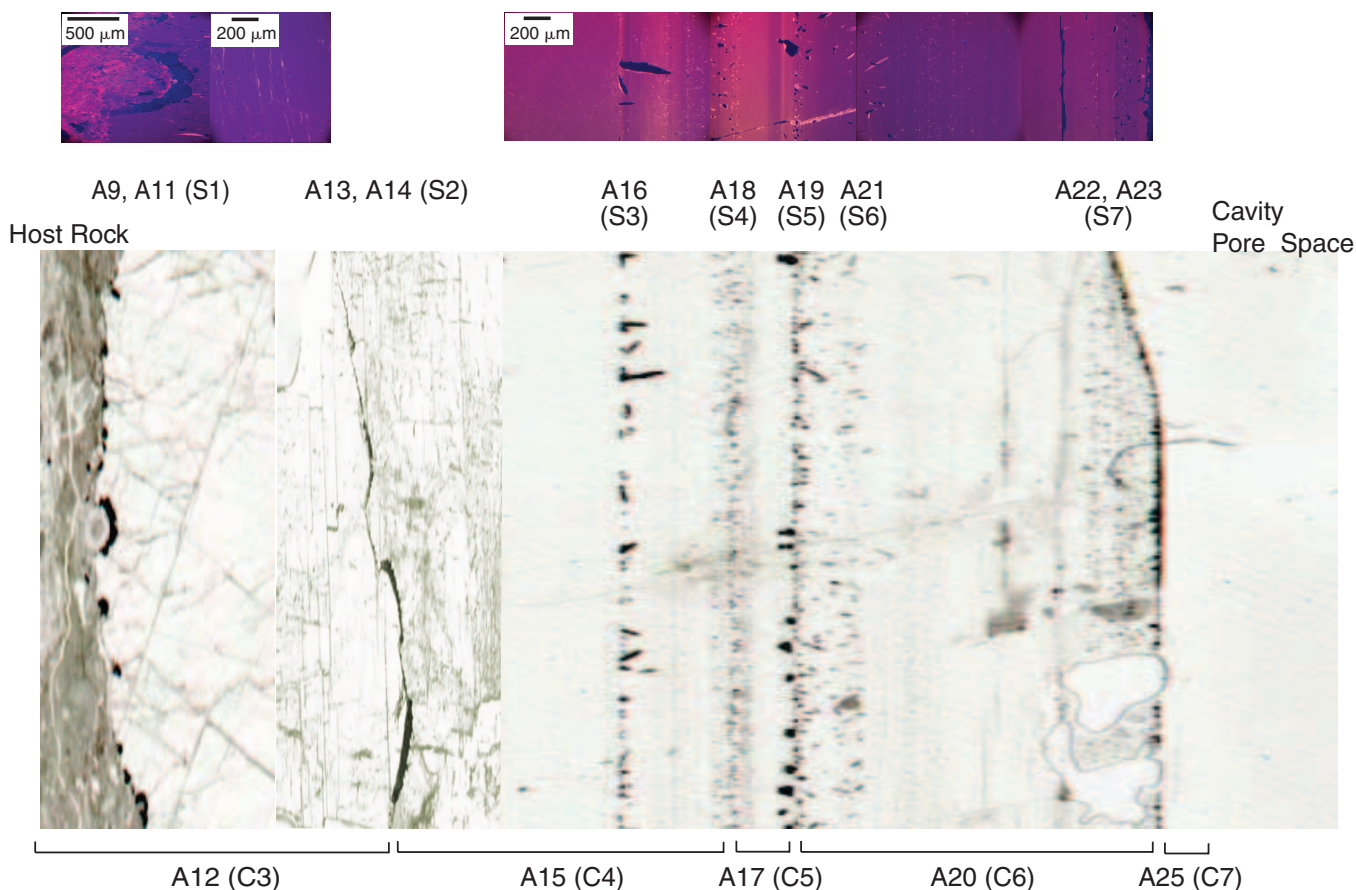


Figure 13 Scanned images of thin sections and correlating cathodoluminescent images reflecting underexaggerated lateral cross section from host rock-cavity dissolution boundary through the cavity cements. All cavity sulfide and calcite zones are represented in cross section.

associated with these dissolution zones (Figure 10e). Planar and subplanar dolomites along dissolution zones are later partially replaced by sulfide cement (S1) A11 (Figure 10e), followed by calcite cementation (C3) A12 (Figure 10e). All fractures (Figure 12a) and dissolution zones (Figure 10e), including the solution cavity, are partially cemented with sulfide cement (S1) A11 (Figures 10e, f) and completely cemented by calcite cement (C3) A12 (Figure 10e, f; Figure 12a, b and Figure 13) postdissolution.

The solution cavity is host to multiple generations of diagenetic events (Figure 13) consisting of distinctive sulfide cements (Figures 13 through 18), calcite cements (Figure 13), and dissolution (Figure 13). Post dissolution (A9), after solution cavity formation, the first cement precipitate is the sulfide zone (S1) A11 (Figures 10f and 14), followed

by the precipitation of the calcite zone (C3) A12 (Figures 10f and 13). “Floating” clasts of host rock are commonly found along the dissolution boundary of the solution cavity and are partially cemented with sulfide cement (S1) A11 and completely cemented by calcite cement A11 (Figure 10f).

Sulfide zone (S1) A11 (S-1, Figure 14) is composed of marcasite (S-1, Figure 16), which is the first sulfide to precipitate followed by epitaxial pyrite (S-1', Figure 16). Marcasite crystals are tabular to prismatic, typically are twinned, and commonly have irregular or distorted habits. The marcasite forms a partial coating over the host rock up to 300 μm thick but is not continuous along all limestone surfaces of the cavity. Epitaxial pyrite habits include octahedrons and pyritohedrons.

Calcite zone (C3) A12 follows precipitation of the sulfide zone (S-1) A11 and is the thickest cement precipitated within the cavity, ranging in thickness from 38 to 102 cm. The calcite zone is very blocky, is highly fractured, and has a yellow to cloudy white color with limited luster and clarity. A12 (C3) first precipitates as a yellow color and grades into a more cloudy white color near the end. Overall, A12 (C3) maintains a low dark purple CL intensity (Figures 11d and 13).

A12 (C3) is terminated by dissolution surface A13 and deposition of sulfide zone (S2) A14 (S-2, Figures 13 and 14). A14 (S2) begins with marcasite precipitation on the dissolution surface of A12 followed by epitaxial pyrite (S-2, Figure 16). A14 forms a continuous coating of 350-μm-thick marcasite over A12 (C3). The coating consists primarily of irregular, twinned, flattened rhombic prisms

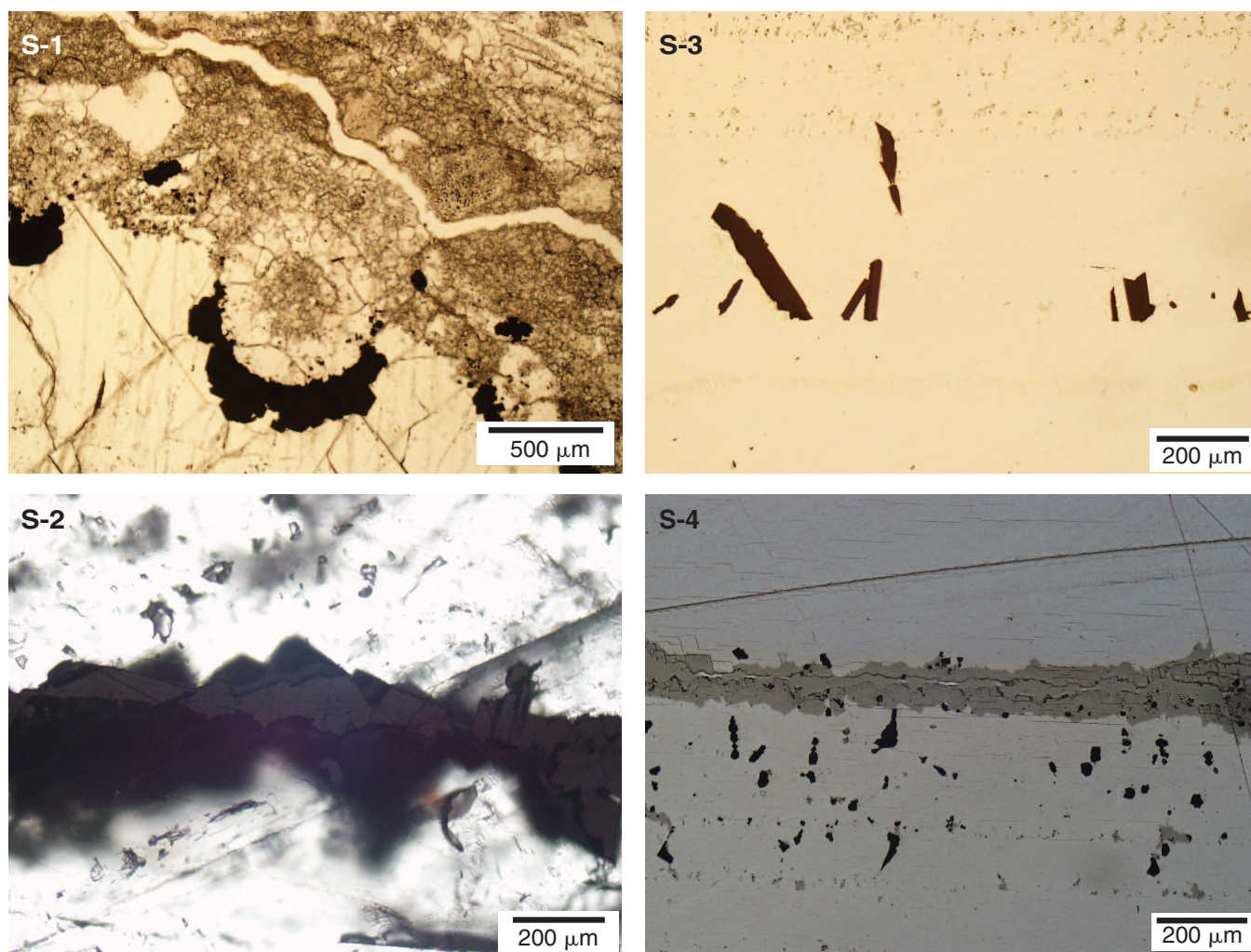


Figure 14 Plane-light photomicrographs of sulfide zones S1 through S4 within the cavity (Figure 13). S-1, the first and earliest sulfide cement (S1) A11 partially coating host rock-cavity dissolution boundary; S-2, sulfide cement (S2) A14 precipitated on A13 dissolution surface of calcite cement (C3) A12; S-3, sulfide crystals (S3) A16 precipitated along symmetric crystal growth plane of calcite zone (C4) A15; S-4, multiple zones of sulfide crystals precipitated along symmetric growth planes of calcite zones (C4 and C5) A15 and A17.

of marcasite growing laterally over A12 (C3). Some marcasite clusters are examined growing over the coating; these consist of large clusters of irregular, tabular rhombic prisms (S-2, Figure 16). Epitaxial pyrite exhibits pyritohedrons and octahedron habits (S-2', Figure 16). All pyrite crystals are approximately 50 μm long.

A14 (S2) is followed by the precipitation of calcite zone (C4) A15 (Figure 13), which ranges in thickness from 10 to 35 cm. A15 (C4) is very blocky and fractured; it is more yellow at the beginning of the zone and ends up with a more

cloudy white color near the end. Relative to A12 (C3), A15 (C4) is not terminated by a dissolution surface, but instead is divided by multiple zones of sulfide precipitates (S3 and S4) A16 and A18 (S-3, Figures 13 and 14) and CL variation with the overlying calcite cement (C5) A17 (Figure 13). A15 maintains a steady moderate to low purple-red CL intensity until precipitation of A16 where it gradually increases in intensity before the precipitation of sulfide zone (S4) A17 where intensity decreases slightly (Figure 13).

Sulfide zone (S3) A16 is the first sulfide that is concentrically zoned along the

calcite growth plane (S-3, Figures 13 and 14). A16 (S3) marks the beginning of the euhedral calcite crystal growth and is the first sulfide to precipitate within the crystals (Figure 7b). A16 (S3) is composed primarily of marcasite, exhibiting well-formed blades to irregular cockscomb blades (S-3, Figure 16). Epitaxial pyrite cuboctahedrons are common on well-formed marcasite blades and bars (S-1', Figure 16). All cuboctahedrons are approximately 20 μm in length. A16 (S3) exhibits iridescence under close examination of the hand-sample specimens (Figure 7). A16 is approximately 400 μm thick.

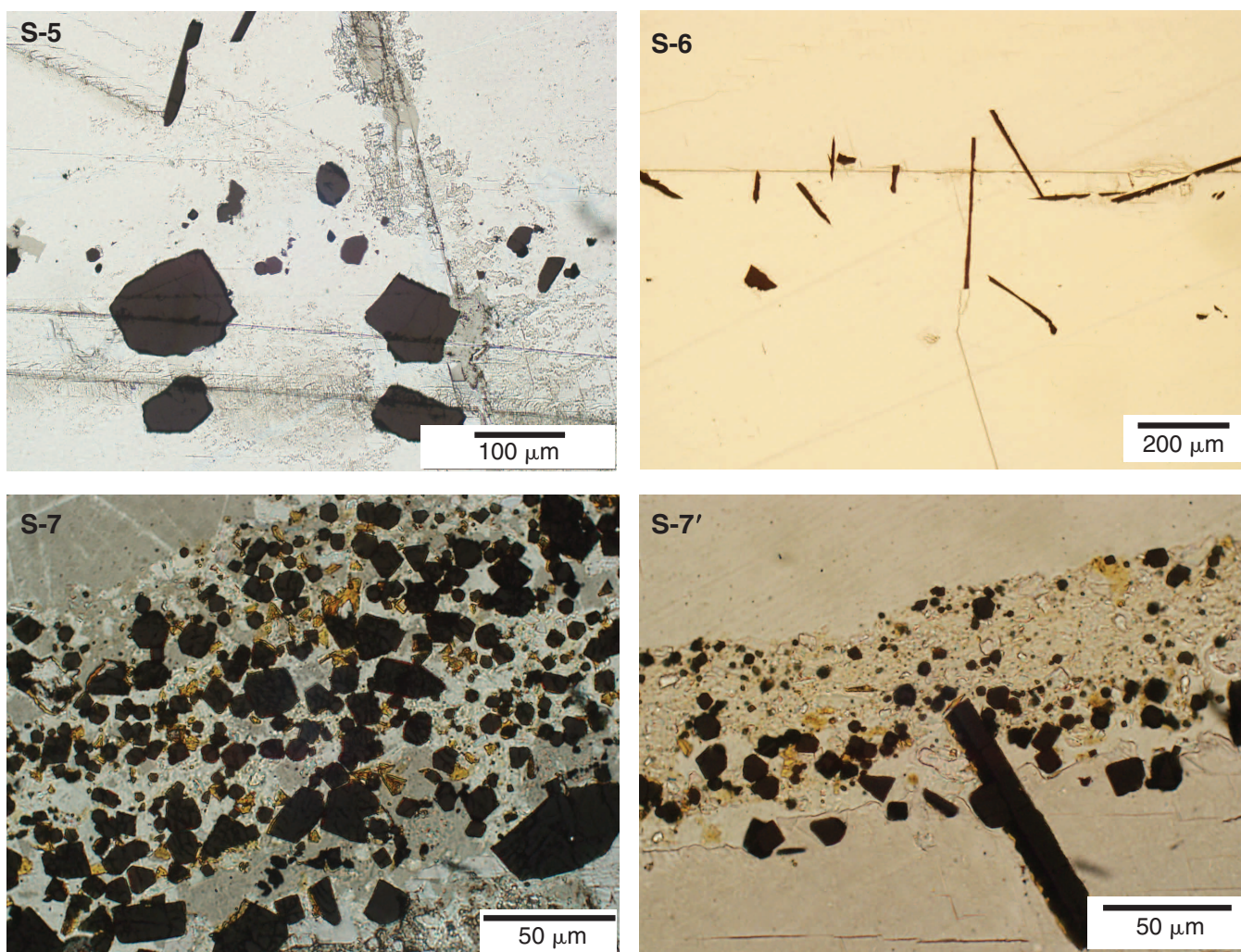


Figure 15 Plane-light photomicrographs of sulfide zones S5 through S7' within the cavity (Figure 13). S-5, sulfide zone (S5) A19 is precipitated along a symmetric growth planes of calcite zones (C5 and C6) A17 and A20 and consists of blocky and elongated irregular sulfide crystals; S-6, sulfide zone (S6) A21 is precipitated along symmetric growth planes of calcite zone (C6) A20 and consists primarily of acicular to filament form sulfide crystals; S-7 and S-7', the last sulfide zone (S7) A23 is precipitated along symmetric growth planes of calcite zone (C6) A20 and on a dissolution boundary at the top of A20. A23 starts as irregular, elongated crystals and grades to mostly blocky crystals. Slightly curved, orange siderite crystals are precipitated over blocky sulfide crystals.

Sulfide zone (S4) A18 marks the end of calcite zone (C4) A15 and the precipitation of calcite zone (C5) A17. A17 (S4) is composed of multiple sulfide zones less than 100 μm long and grouped together, forming a zone of sulfides approximately 500 μm thick (S-4, Figure 14). A17 (S4) is characterized primarily by stacked and skewed pyrite octahedron verticals (S-4', Figure 17). These stacked octahedrons or chains of octahedrons range from 50 to 300 μm in length and are typically about

25 μm wide. Many of these octahedron stacks are skewed and appear stretched (S-4', Figure 17). Trace tabular and irregular marcasite rhombic prisms are also found throughout S-4. Calcite zone (C5) A17 is approximately 600 μm thick and is characterized by a relatively high CL intensity; however, at approximately 150 μm from the top of the A17 (C5), there is a noticeable lower CL intensity zone (Figure 13). Calcite zone (C5) A17 is clear and has very high luster. A17 is a transition zone between smaller sulfide crys-

tal precipitates in sulfide zone (S4) A18 (S-4, Figure 14) at the base of A17 and large sulfide crystal precipitates at the top of sulfide zone (S5) A19 (S-5, Figure 15) at the top of A17 (Figure 13).

Sulfide zone (S5) A19 contains primarily pyrite crystals and is characterized by larger pyrite crystals, all approximately 150 μm thick at the base of A19 (S-5, Figures 13 and 15). A19 grades upward into clusters of pyrite pyritohedrons, octahedrons, and pyrite bars (S-5, S-5', Figure

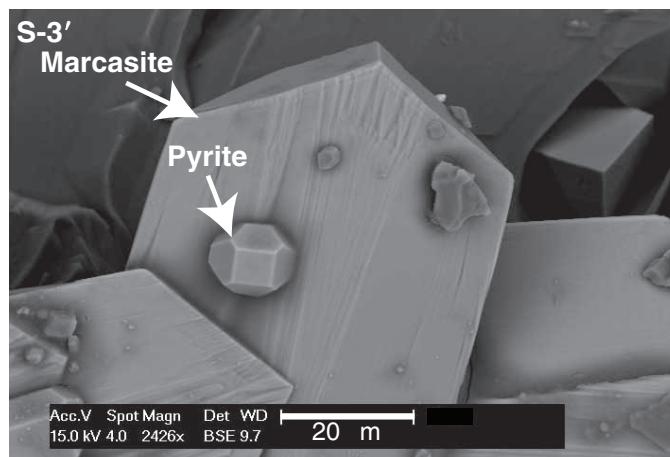
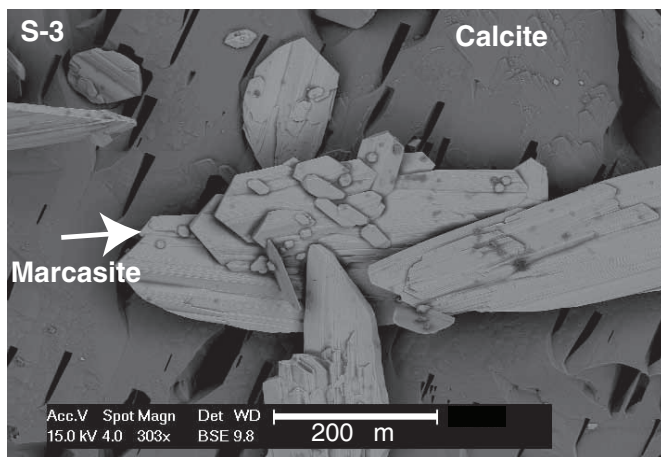
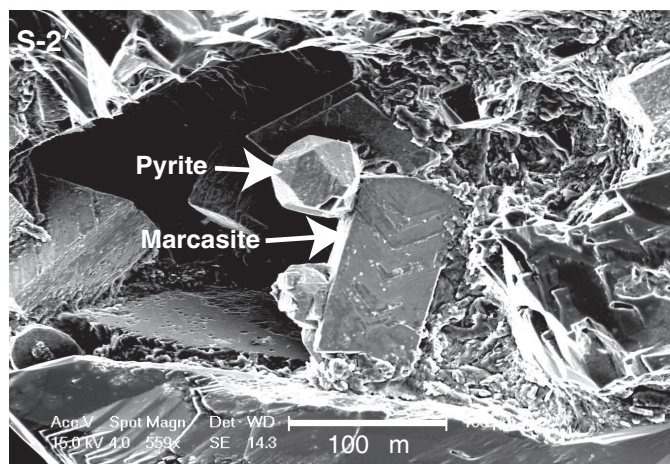
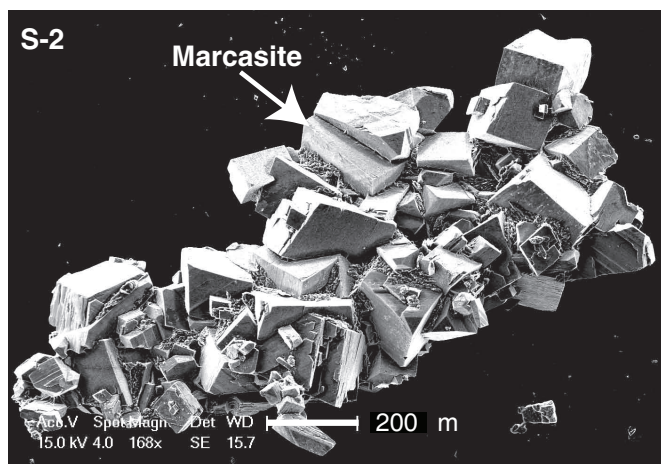
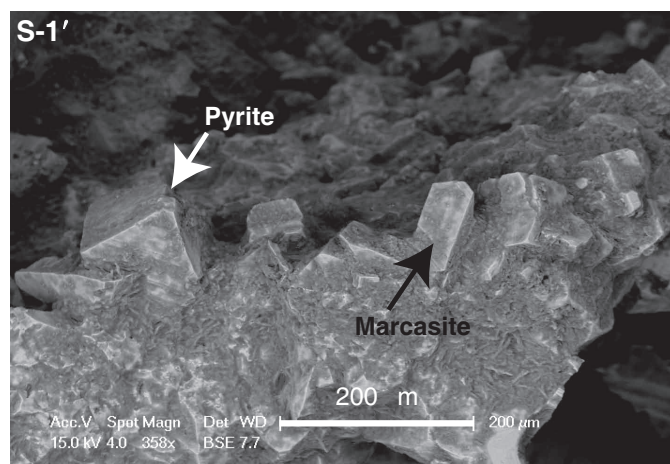
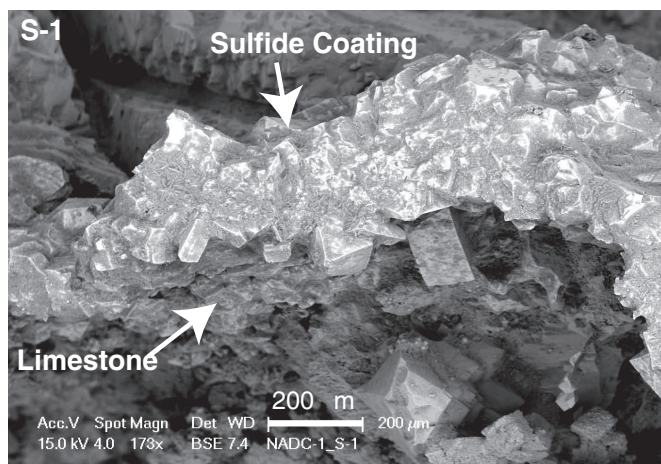


Figure 16 Environmental scanning electron microscopy back-scattered photomicrographs displaying cavity sulfide zones S1 through S3. Brighter emission surface represents sulfides and darker emission surface represents calcite. S-1 and S-1', sulfide cement (S1) A11 partially coating host rock; marcasite grows as a mostly irregular coating with later epitaxial pyrite octahedrons; S-2 and S-2', sulfide cement (S2) A14 consists of a heavy coating of irregular, tabular, and rhombic prisms with later epitaxial pyrite pyritohedrons and octahedrons; S-3 and S-3', sulfide cement (S3) A16 consists of spaced out bladed marcasite with later epitaxial pyrite cuboctahedrons.

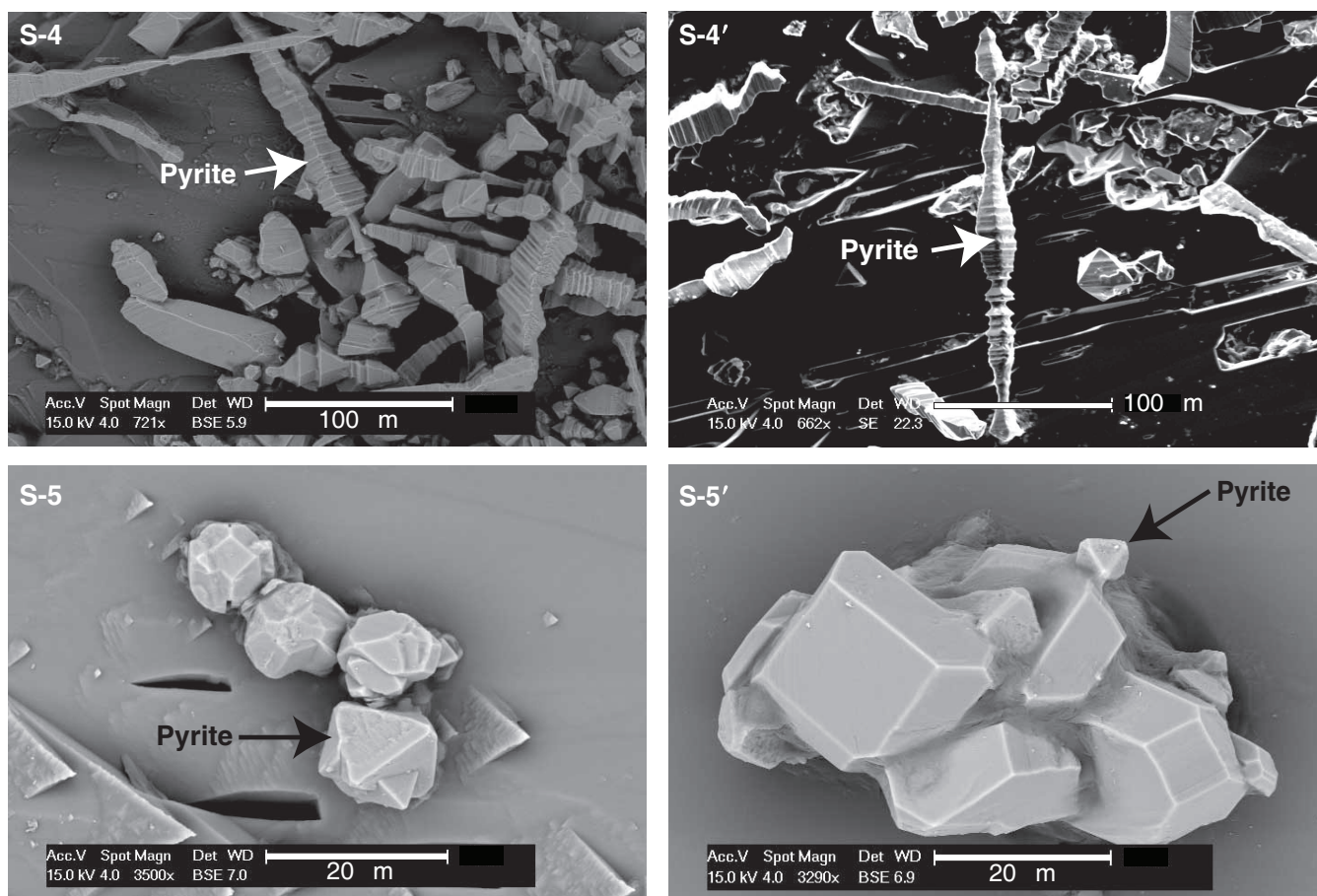


Figure 17 Environmental scanning electron microscopy back-scattered photomicrographs displaying cavity sulfide zones S4 and S5. S-4 and S-4', sulfide zone (S4) A18 exhibits stacked and stretched pyrite octahedron verticals and trace irregular marcasite rhombic prisms. S-5 and S-5', sulfide zone (S5) A19 consists primarily of pyrite octahedrons and pyritohedrons and trace marcasite.

17). As A19 (S5) crystals fine upwards, CL intensity decreases in calcite zone (C6) A20 (Figure 13). Sulfide zone (S5) A19 is approximately 450 μm thick. Another sulfide zone (S6) A21 (S-5, Figure 15) at the base of A20 (Figure 13) is identified based on morphological differences compared with A19 (S-6, Figure 15). Sulfide zone (S6) A21 is characterized by needle-like sulfide crystals in the hand sample (Figure 7) and thin section (S-6, Figure 15). The needle-like or filamentous form crystals in A21 have little to no symmetry (S-6, S-6', Figure 18). The XRD analysis suggests that the needles are marcasite (S-6, Appendix). Epitaxial pyrite pyritohedrons and cuboctahedrons are common on these

sulfide needles. Sulfide zone (S6) A21 is approximately 400 μm thick.

Calcite zone (C6) A20 is the last zone of calcite that includes sulfides (Figure 13). A20 begins at the top of sulfide zone A19 and continues through A20 until termination by a slight dissolution zone at the base near the top of sulfide zone (S7) A21 (S-7', Figure 15). Throughout the middle zone of A20, numerous zones of <10- μm -thick pyrite are included but were undifferentiated (Figure 13). Also, numerous zones of <50- μm -thick marcasite and pyrite are included near the top 600 μm of A20 and are grouped together as sulfide zone (S7) A7. A20 is characterized by mostly low intensity CL, especially near the base and end (Figure 13). The CL increases in inten-

sity just before precipitation of sulfide zone (S7) A23 but decreases in intensity during precipitation of A23 (S7), increases again, and then decreases at the very end of A23 (S7) precipitation (Figure 13). A20 is approximately 4 mm thick.

The base of A23 (S7) is dominated by irregular blades and tabular rhombohedrons of marcasite (S-7, Figure 18). The largest marcasite crystals are approximately 380 μm , but most average around 200 μm . All marcasite crystals are suspended in calcite zone (C6) A20. Epitaxial pyrite octahedrons are common on irregular marcasite crystals. A23 (S7) grades upward from marcasite to pyrite crystals. Pyrites are

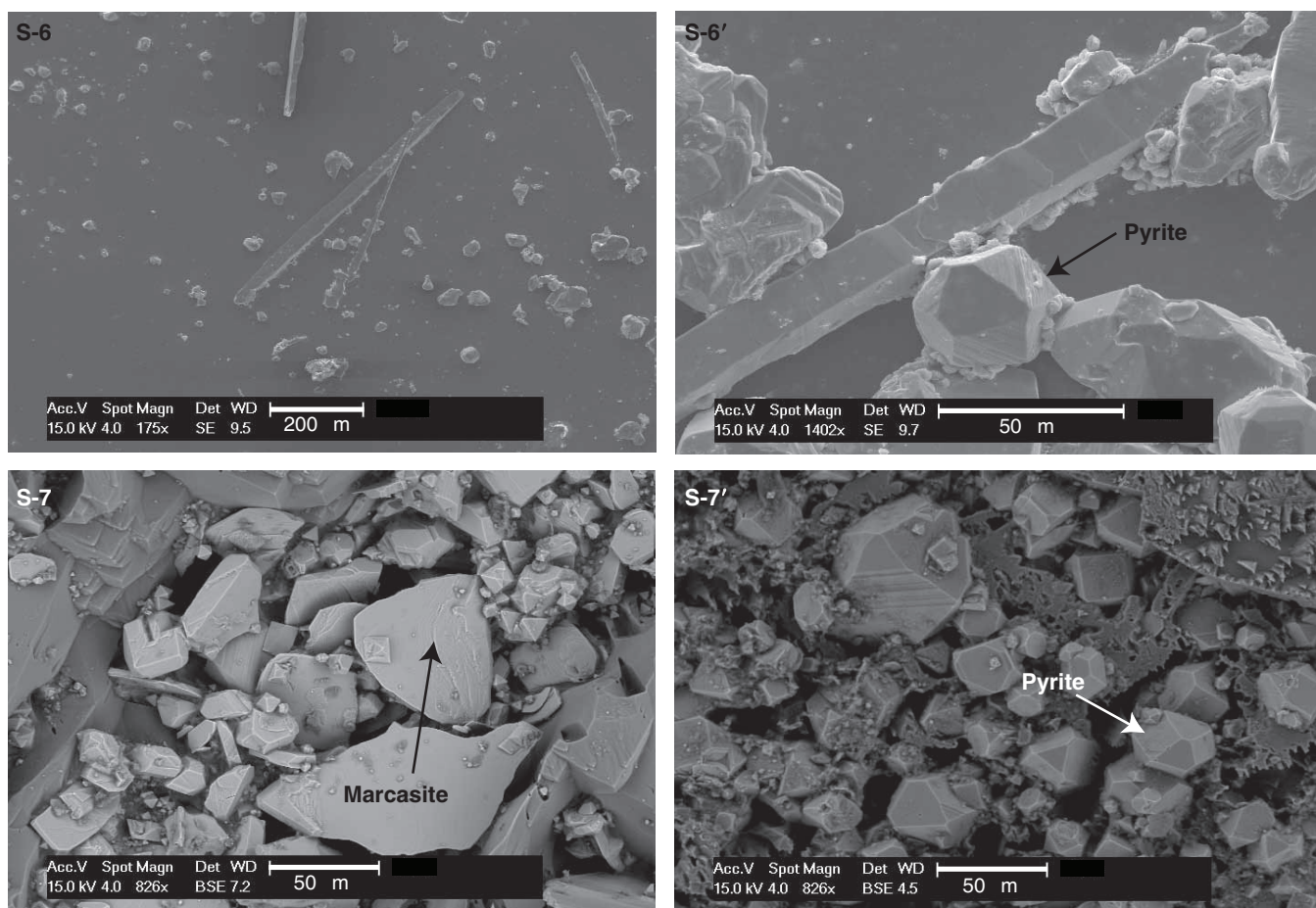


Figure 18 Environmental scanning electron microscopy back-scattered photomicrographs displaying cavity sulfide zones S6 and S7. S-6 and S-6', sulfide cement (S6) A21 consists of elongated filamental crystals with epitaxial pyrite pyritohedrons; it is unclear if filaments are pyrite or marcasite; S-7 and S-7', sulfide cement (S7) A23 exhibits irregular marcasite blades that grade up into pyrite pyritohedrons, octahedrons, and cuboctahedrons.

precipitated at the top of A20 on a slight dissolution surface A22 (S-7', Figure 16). Pyrites could be grouped into their own paragenetic event; however, they are epitaxial with and closely related to the marcasite suspended in calcite A20 (C6) and therefore were grouped in A23 (S7). Pyrites exhibit octahedral, pyritohedral, and cubic habits (S-7', Figure 18). Trace oxidized siderite rhombohedrons with curved faces are common precipitates around pyrite in sulfide zone (S7) A23 (S-7, S-7', Figure 15). Pyrite and siderite are cemented with calcite cement (C7) A25.

Calcite zone (C7) A25 is a 0.5- to 2-cm-thick calcite layer that forms a partial coating over A23 (S7) and cements the

top of A23 along the dissolution boundary A22. It is the outermost cement over every euhedral crystal lining the cavity (Figure 7). In the solution cavity, A25 (C7) is thickest on the lateral and base sides of the crystal face, inward toward the center of the solution cavity. A25 (C7) is not found on the top of the protruding euhedral crystals (Figure 7). A25 (C7) forms sharp crystal faces and symmetric and asymmetric geometries. Some crystal faces appear stretched with sharp but curved edges. A25 (C7) is extremely lustrous, although some crystal faces are slightly etched, dulling the luster and exhibiting a frosty white color. Pitting caused by dissolution event A26 is common on the lustrous crystal faces of A25 (C7) cement and exhibits internal crystal geometries.

Geochemical Analyses

The isotopic and trace element composition of the calcite and sulfide solution cavity cements that constitute the paragenetic sequence following the formation of the solution cavity is presented in Table 2. Based on the elemental abundance results for calcite cements, A15 (C4) was reported as two distinct cements; C4 and C4'. The most distinct geochemical characteristics of the diagenetic cementation events are (1) high Mg concentrations (1,113 to 1,615 ppm) in earlier calcite cements (C3 and C4) A12 and A13 relative to lower concentrations (395 to 526 ppm) for later calcite cements (C4' to C7); (2) more radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for earlier calcite cement

Table 2 Elemental and isotopic abundances of the solution cavity cements.

Paragenetic sequence	Ca (mol%)	Na (ppm)	Sr (ppm)	Fe (ppm)	Mg (ppm)	Mn (ppm)	⁸⁷ Sr/ ⁸⁶ Sr (standard SRM976)	δ ¹³ C (VPDB)	δ ¹⁸ O (VPBD)
Cavity calcite									
A12 (C3)	40.7	47	164	355	1,113	238	NA	−1.95 −1.89 −1.62	−7.10 −6.99 −7.35
A15 (C4)	40.0	52	150	77	1,615	566	0.71015	−2.20 −2.13	−5.05 −4.22
A15 (C4')	40.5	44	196	242	395	372	NA	−4.24 −3.60	−6.13 −4.62
A17 (C5)	40.6	64	23	bd	490	451	NA	−4.63 −4.88 −4.73	−3.47 −3.37 −3.55
A20 (C6)	40.4	43	155	146	375	203	0.70980	−3.53 −3.27 −3.44	−8.86 −9.27 −9.24
A25 (C7)	41.0	147	149	bd	526	158	0.70898	−8.57 −10.58 −8.57	−6.31 −8.44 −6.18
	Fe (mol%)	S (mol%)	Cu (ppm)	Pb (ppm)	Zn (ppm)				
Cavity sulfide									
A11 (S1)	46.3	50.7	376	bd	bd				
A14 (S2)	NA	NA	NA	NA	NA				
A16 (S3)	45.4	51.1	87	2,172	423				
A18 (S4)	46.2	51.1	44	889	0				
A19 (S5)	45.4	51.3	144	6,013	767				
A21 (S6)	45.2	51.4	29	4,203	0				
A23 (S7)	46.4	51.5	694	0	110				

¹Abbreviations: VPBD, Vienna Pee Dee Belemnite laboratory standard; bd, below detection level; NA, not available at time of analysis.

(C4) A15 relative to ⁸⁷Sr/⁸⁶Sr ratios (0.70980 to 0.70898) of later cements (C6 and C7) A20 and A25; (3) two distinct trends of δ¹³C VPBD and δ¹⁸O VPBD correlating to the paragenetic events and following a similar pattern of δ¹³C VPBD getting lighter and δ¹⁸O VPBD getting heavier with respect to time (Figure 19); (4) high concentration of Na (147 ppm) and Sr (249 ppm) in the latest calcite cement (C7) A25; and (5) high Pb concentrations (889 to 6,013 ppm) in sulfide cements (S3 through S6) A16 through A23 and relative Zn concentrations (110 to 767 ppm) in sulfide cements (S3, S5, and S7) A16, A19, and A23. The XRD analyses of sulfides indicate that they are all composed primarily of marcasite (Appendix). Pyrite was indicated by XRD in zones S1, S5, S6, and S7; however,

high-resolution examination using an ESEM confirms that pyrite exists in all of the sulfide zones.

DISCUSSION

Depositional History of the Solution Cavity Host Rock

The solution cavity at the Conco Mine is located in the upper Ordovician Wise Lake Formation of the Galena Group. The Wise Lake is described as fossiliferous wackestones with thin beds of grainstones deposited in a low-energy, subtidal environment as suggested by Willman and Kolata (1978). The grainstone beds have been attributed to deposition from periodic storm events. The Galena Group rock units have been described in

detail in northern Illinois (Willman and Kolata 1978) and likely maintain uniformity and continuity in sedimentological composition over hundreds of kilometers, further indicating deposition in a shallow marine ramp environment with low sedimentation rates (Kolata et al. 2001). Furthermore, Kolata et al. (2001) suggest that the lack of micrite in southern Illinois and its abundance in northern Illinois are evidence indicating that the Galena Group was deposited more shoreward in warmer waters in northern Illinois than in southern Illinois.

The clay bed noted in the Wise Lake Formation host rock, directly above the present-day solution cavity, is probably equivalent to the Dygerts K-bentonite bed described by Willman and Kolata

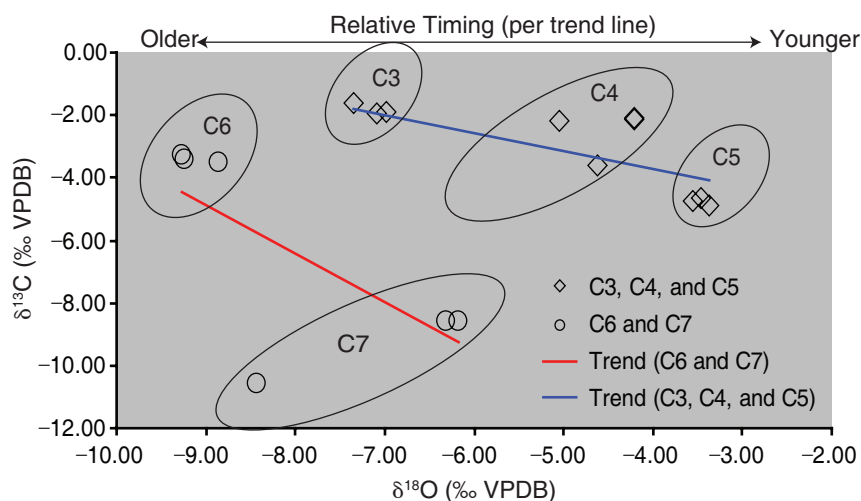


Figure 19 The $\delta^{18}\text{O}$ VPDB values of cavity calcite zones C3 through C7 compared with their ^{13}C VPDB values. Two distinct trend lines are indicated for zones C3 through C5 and C6 through C7. Because calcite zones are labeled by their paragenetic event ordering, isotopic values of calcites on each trend line are getting lighter ^{13}C VPDB and heavier $\delta^{18}\text{O}$ VPDB with respect to time. This isotopic comparison suggests at least two different fluids were responsible for precipitation of calcite cements within the solution cavity.

(1978). A previous study near the Conco Mine (Graese 1991) notes that the Dygerts K-bentonite bed lies approximately 24 to 30 m below the top of the Wise Lake Formation, which is consistent with the depth of the clay bed observed above the solution cavity and approximately 28 m below the top of the Wise Lake Formation. The Dygerts K-bentonite bed (originally volcanic ash) is thought to be the product of volcanoes situated in an island arc system in the Appalachian mobile belt (Kolata et al. 1986). Burrowing is not apparent in host rock below the clay bed at the studied solution cavity; however, mineralized burrows inside other cavities below the bentonite zone indicate that burrows are not confined to beds above it. Similarly, it is well noted that the Galena-Platteville throughout the region is highly burrowed and bioturbated and is commonly described as mottled due to the color appearance of preferentially dolomitized burrows (Kendall 1977, Willman and Kolata 1978). Burrows in host rock above bentonite terminate at the top of it. This volcanic ash bed, composed of fine-grained glass, may have deterred burrowing by marine organisms. Thus, the early bentonite may have acted as a

barrier for downward burrowing organisms and later as an impermeable aquitard for upward migrating fluids.

Diagenetic History

The combination of petrographic, ESEM, and geochemical evidence suggests that diagenetic alteration of host rock and the formation of the solution cavity and mineral cements occurred in two major events: (1) early-stage diagenesis and (2) late-stage diagenesis. This study focuses primarily on late-stage diagenesis, which includes solution cavity formation and subsequent cementation and alteration events. Late-stage diagenesis is discussed in two contextual groups: (1) fracturing and dissolution and (2) sequences of dissolution, sulfide precipitation, and calcite precipitation. The fracturing of the host rock is directly followed by fracture-focused dissolution, indicating that the fractures at Conco were the significant conduits for fluid transport. However, the sedimentological and stratigraphic context of the cavity (i.e., overlying clay bentonite bed and mineralized burrows in other cavities) suggests that stratigraphic facies strongly influenced fluid flow dynamics and resulting water-rock interactions.

Furthermore, fracture-focused fluids diagenetically altered surrounding host rock. The process of host rock dissolution, sulfide cement precipitation, and calcite cement precipitation is repeated several times within the solution cavity. Geochemical and high-resolution microscopic analysis of these mineral precipitation events suggest that they were caused by changes in the geochemical composition and extent of reaction within the diagenetic system.

Early-Stage Diagenesis

Early diagenetic alteration consists of paragenetic events A2 to A7 (Figure 8) (Table 1). Depending on the original sedimentological composition of the host limestone, wackestone and grainstone fossils either (1) are dissolved (A2) and later cemented by calcite cement (C1) A3 (Figure 9a) or (2) partially retain their original structure due to conversion to neomorphic calcite (C1) A3 (Figures 9a, c) as exhibited by dull, low intensity CL (Figure 9c). A similar CL color of internal fossil structure and blocky calcite cement in dissolved fossil interiors imply that calcite's (C1) A3 are related and formed diagenetically early rather than being primary (Figure 9c, d). Burrowing (A4) of grainstone (Fig 10c) likely occurred before or during calcite alteration and cementation (C1) A3; however, these events are paragenetically undifferentiated. Burrows are cemented by nonplanar dolomites A6 (Figure 10b). A3 calcite and A6 dolomites are also paragenetically undifferentiated. It might be expected that the early calcite cement (C1) A3 would tightly cement the burrow if A3 precipitated. However, burrowing likely resulted in a higher permeability and may have therefore acted as a sink for organic matter and clay that later enhanced dolomite precipitation (Fouke et al. 1996, Gingras et al. 2004). In this case, burrow dolomites precipitate after A3. A microcrystalline dolomite (A5) that partially replaces wackestone matrix (Figure 10a) is indistinguishable in PL and CL from cement A6. Calcite cement (C2) A7 is described primarily as a syntaxial cement over calcite cement (C1) A3 and appears to surround the burrow without a crosscutting relationship, suggesting A7 (C2) precipitated after burrow dolomites A6 (Figure 10c).

Late-Stage Diagenesis

Fracturing and Dissolution

Microfractures (A8) crosscut the host rock wackestone matrix as well as the fossil fragments replaced and cemented by calcite (C1 and C2) A3 and A7 (Figure 11a), which indicates that fracturing of the host rock postdates precipitation of calcite cements (C1 and C2) A3 and A7. The CL of calcite cements in host rock microfractures (Figure 11c) are comparable to CL of early cavity calcite cements (C3) A12 (Figure 11d), suggesting that microfractures are cemented by calcite (C3) A12. A12 cementation around grains relative to the fractures (Figures 11a, c) suggests slight dissolution along microfractures; however, most dissolution (A9) occurs along larger fracture networks generally trending northwest-southeast (Figure 4), resulting in the formation of meter-scale solution cavities (Figure 5). Preferential dissolution along northwest-southeast fractures rather than other prominent northeast-southwest fractures at Conco Mine may be indicative of continental compressional stress at the time of cavity formation. Daniels et al. (1990) suggested that mineralogical and chemical differences in authigenic clays found in orthogonal joint sets formed in the eastern Appalachian Basin during Alleghenian orogenic deformation (Permian) were related to permeability variations controlled by the orientation of the Alleghenian stress fields. They suggested that joint sets that were oriented roughly perpendicular to the maximum paleostress direction (northeast-southwest) were compressed during the Allegheny Orogeny, while joint sets oriented roughly parallel to the maximum stress direction (northwest-southeast) were opened. The opening of these joint sets increased permeability, promoting fluid flow through the joints and encouraging diagenesis along fractures. This process would explain the majority of the solution structures found at Conco Mine that are roughly oriented along northwest-trending fractures or joint sets, further suggesting that fluid flow initiated during or after the Allegheny Orogeny (Permian). It has been noted that regional-scale fracturing was likely the most important process for

creating conduits for fluid transport and subsequent deposition of MVT minerals (Garven et al. 1993). A similar process was likely possible at Conco as indicated by the fracture-focused meter-scale cavities and mineral precipitates throughout the Conco Mine (Figures 4 and 5). Furthermore, the vertical geometry of the cavity and the lenticular geometry at the top of the cavity (Figure 5) where it terminates at the B1 clay bed (Figure 12) suggests that fluid ascended up vertical open fractures where it was impeded at the clay bed acting as an aquitard, forcing lateral fluid flow and associated dissolution.

Millimeter- to micrometer-scale dissolution (A9) of the slightly fractured host rock predates later planar to subplanar dolomite A10 (Figure 10 D). The distribution of A10 dolomites along these millimeter- to micrometer-scale dissolution zones constrains the timing of this late-stage dolomitization event. A10 dolomites are always slightly replaced by sulfide cement (S1) A11 and completely cemented and occasionally “floating” in calcite cement (C3) A12 (Figure 10d). Clasts of host rock are also found “floating” in calcite cement (C3) A12 and typically replaced by sulfide cement (S1) A11 (Figure 10), which may imply that the diagenetic fluids that caused varying degrees of dissolution are genetically related to A10 dolomitization, A11 sulfide precipitation, and A12 calcite precipitation. There is no evidence that floating or cemented dolomite grains and host rock clasts are a product of brecciation, but instead may have a co-genetic relationship of the dolomitizing, dissolving, and calcite precipitating fluids. Furthermore, Mg concentration (1,113 ppm) in A12 (C3) is substantially higher than most late-stage calcites (C4' to C7; Table 2), suggesting that the early diagenetic fluids responsible for dissolution were evolving, eventually reaching the Mg supply needed to precipitate dolomite (Land 1985) and subsequently precipitate A11 iron sulfides and A12 calcite. However, only trace amounts of dolomite are found within these micro-dissolution zones of host rock and are virtually nonexistent along the dissolution surface of the solution cavity-host rock dissolution boundary.

The Sequence of Dissolution, Sulfide Precipitation, and Calcite Precipitation

The diagenetic fluids that created the solution cavity presumably were strongly buffered by the host rock and later chemically evolved to precipitate sulfide cement (S1) A11 and later calcite cement (C3) A12 (Figures 10f and 13), which indicates a repeating history of fluid chemistry oscillation from calcite undersaturation to sulfide and calcite oversaturation (repeated from the beginning of the A9 solution cavity formation through last A26). Previous studies have interpreted this evidence to represent distinct pulses of upwelling subsurface waters (Cathles and Smith 1983, Deloule and Turcotte 1989) transported through fractures and compositionally evolving over time. Furthermore, the mixing of multiple fluid types (the “mixing hypothesis”) (Beales and Jackson 1966, Anderson 1983, Sverjensky 1986) may be another controlling factor in this sequence of diagenetic events. The mixing model proposes that MVT sulfide precipitation is the result of a metal-bearing fluid such as hydrothermal brine migrating from deep to shallow. These basinal waters mix with formation waters rich in H_2S , resulting in the precipitation of metal sulfides. However, the mixing model may not account for the dissolution of the host rock. Anderson (1983) suggested that the mixing of a reduced sulfur-bearing solution and metal-bearing solution theoretically reduces the saturation state and dissolves carbonate minerals. However, the opposite is observed at Conco, where dissolution is followed by sulfide and calcite precipitation, as indicated by the paragenetic sequence (Figure 8).

The mixing of two solutions with different compositions, each of which is in equilibrium with respect to calcite, has been shown to result in calcite dissolution and precipitation (Wigley and Plummer 1976, Rimstidt 1997, Anderson 2008). Corbella et al. (2004) conducted reactive transport modeling and calculations for the mixing of two fluids to account for the dissolution of host rock and the precipitation of sulfides and calcite. In these experiments, reduced sulfur-rich groundwater and reduced metal-rich brine (both saturated with

respect to calcite) resulted in both dissolution and precipitation of sulfide and calcite cement. Corbella et al. (2004) also found that when the host rock pore water contains H_2S , and the brine contains dissolved zinc (or iron), sulfide cement is precipitated, and dissolution occurs due to sulfide-induced lowering of pH (Anderson and Thom 2008). As previously mentioned, this does not appear to be the case at Conco Mine.

An interesting observation is the precipitation of marcasite followed by epitaxial pyrite, which may suggest that the fluid responsible for dissolution, sulfide precipitation, and calcite precipitation contained a bulk solution pH that was increasing as a function of time. This explanation is supported by experiments that suggest that the pH of precipitant fluid differs substantially for marcasite and pyrite. Marcasite precipitation is strongly favored in a more acidic (pH approximately 4 to 5) solution, and pyrite is favored in less acidic solutions (Murowchick and Barnes 1986; Schoonen and Barnes 1991a, 1991b, 1991c). Thus, compositional shifts in the pH of the diagenetic waters are suggested by sequential mineralization events in the solution cavity, including sulfide cementation event (S1) A11 and all the other sulfide cementation events (S2–S7; Figure 8) consisting of marcasite and epitaxial pyrite followed by calcite co-precipitation. These changes may be explained by fluidization events consisting of acidic and possibly undersaturated brines that are compositionally changing as a result of water-rock interaction (dissolution) or mixing with formation waters.

The first solution cavity diagenetic sequence of A9 dissolution, A11 sulfide precipitation, and A12 calcite precipitation is followed by a second sequence consisting of A13 dissolution, A14 sulfide precipitation, and A15 calcite precipitation (Figures 8 and 13). Although the extent of A13 dissolution is unknown, the volume of burial water involved in the reaction must have been less than that of the A9 dissolution event that formed the cavity. Also, the amount of calcite deposited in cementation event A15 is less than A12 (Table 1). Similar to the first sequence sulfide cement (S1) A11, sulfide cement (S2) A14 is composed

of marcasite followed sequentially by pyrite precipitation; however, the amount of precipitated sulfides is comparable. Although, based on the amount of dissolution and calcite precipitation, the second sequence (A13, A14, and A15), underwent less reactive fluidization or reached saturation faster than the first sequence (A9, A11, and A12).

The last sequence of diagenetic events in the cavity is similar to the first two, except, importantly, it is in reverse order. Near the end of calcite cement (C6) A20 precipitation, marcasite begins to co-precipitate within the sulfide cementation event (S7) A23. The size of marcasite cements then increase (Figure 13) until a dissolution event (A22) occurs. Sulfide cementation continues with a change to the epitaxial precipitation of pyrite cement over marcasite cement as well as the dissolution surface (S-7, S-7', Figure 15). Calcite (C7) A25 and A24 siderite cements precipitate co-genetically with the A23 pyrite crystals. This paragenetic sequence (A20 calcite cement, A23 sulfide cement [marcasite], A22 dissolution, A23 sulfide cement [pyrite], A24 siderite, and A25 calcite cement) is suggestive of fluid pH and saturation state with respect to the sulfides and calcites. A possible mechanism would be the slow influx of slightly acidic brine mixing with oxidizing formation waters.

These three sequences of diagenetic events (Table 1) also exhibit distinct geochemical compositional differences that can be used to interpret the source of the diagenetic fluids. As an example, calcite cement (C4) A15 is physically (Table 1) and chemically (Table 2) similar to calcite cement A12 relative to later calcite cements (C4' through C7). Specifically, the A15 calcite $^{87}Sr/^{86}Sr$ ratios are more radiogenic (0.71015) than ratios for A20 (0.70980) and A25 (0.70898) calcites. This difference suggests that the diagenetic water that precipitated each of these calcites was derived from different sources, as illustrated in the following examples. The $^{87}Sr/^{86}Sr$ ratios of A20 and A25 are consistent with those of Lower to Middle Ordovician seawater (Burke et al. 1982), including the Galena Group formation water in the Illinois Basin (Stueber et al. 1987). However, a newer secular variation in $^{87}Sr/^{86}Sr$ of Ordovician brachiopods reports seawater

$^{87}Sr/^{86}Sr$ decreased from 0.70900 to 0.70780 during Ordovician time (Shields et al. 2003) suggesting that calcite cements A15 and A20 were precipitated from older seawater or diagenetic water with increased radiogenic Sr. The seawater from which calcite cement A25 precipitated would be of Lower Ordovician according to this secular variation curve (Shields et al. 2003). Winter et al. (1995) analyzed the $^{87}Sr/^{86}Sr$ of dolomite cement in the Lower Ordovician St. Peter Sandstone of the Michigan Basin and suggested that four different fluids were involved in dolomitization: Fluid 1, older seawater (0.7093 ± 1); Fluid 2, Ordovician seawater (0.7084 ± 1); Fluid 3, fluid derived from water-rock interaction with potassium feldspar crystals (igneous and/or sedimentary) at the Precambrian-Cambrian contact (0.710 to 0.711); and Fluid 4, derived from water-rock interaction with Silurian gypsum (0.7085 ± 1). The present study's $^{87}Sr/^{86}Sr$ analyses of calcite cement suggest that the diagenetic fluids responsible for the first two sequences of dissolution and mineral precipitation in the Conco solution cavity may have originated from water-rock interaction with arkosic sandstones in the basal Cambrian Mt. Simon Sandstone and/or Precambrian granitic basement rock (Figure 3) (Winter et al. 1995). Later cement precipitation events, such as A25, may have been derived from water-rock interaction with Ordovician or Silurian carbonates and connate burial fluids, as implied by the $^{87}Sr/^{86}Sr$ composition of A25 (0.70898). Less acidic brine or less extensive water-rock interaction events of acidic brine and/or the influence of shallower and less acidic Ordovician or Silurian formation waters might explain the overall lack of dissolution after the precipitation of calcite zone (C3). These shallower formation waters may explain the increased concentrations of Na (147 ppm) and Sr (259 ppm) in the last calcite precipitation event (C7) A25 relative to earlier calcite events (Table 2). Fluids with higher concentrations of Na and Sr may indicate that the fluid interacted with evaporite deposits, such as those in the overlying Silurian bedrock (Figure 3) (Fisher et al. 1988, Winter et al. 1995). Such interaction would indicate that an element of downward flow occurred, probably

farther and deeper in the basin, before being transported up through the dissolved fractures at Conco.

Stable isotope data also support at least two different diagenetic fluids responsible for mineral precipitation at Conco Mine. A crossplot (Figure 19) of the $\delta^{13}\text{C}$ VPBD and $\delta^{18}\text{O}$ VPBD values of calcite cements (C3) A12 through (C7) A25 exhibits two distinct trends: (1) cement (C3) A12 through (C5) A17 increasing in $\delta^{18}\text{O}$ (−7.35‰ to −3.37‰) and decreasing in $\delta^{13}\text{C}$ (−1.62‰ to −4.88‰) and (2) cement (C6) A20 through (C7) A25 increasing in $\delta^{18}\text{O}$ (−9.27‰ to −6.18‰) and decreasing in $\delta^{13}\text{C}$ (−3.27‰ to −0.58‰). With respect to the paragenetic ordering of each diagenetic cementation event within the cavity, each trend line or fluid increases in $\delta^{18}\text{O}$ and decreases in $\delta^{13}\text{C}$ over to time. A study on Upper Ordovician brachiopods from 10 worldwide localities reports $\delta^{18}\text{O}$ values from −3.5‰ to −6.9‰ and $\delta^{13}\text{C}$ from 0.2‰ to 5.8‰ (Shields et al. 2003). These values are reflective of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values for Upper Ordovician carbonates. Calcite events (C3) A12 and (C6) A20 are the first cements of each trend line (Figure 19), and both have $\delta^{18}\text{O}$ values lighter than the range for worldwide Upper Ordovician carbonates. All of the calcite cements (C3 to C7) A12 through A25 have much lighter $\delta^{13}\text{C}$ values than the worldwide Upper Ordovician carbonates, indicating a different source of carbon. The isotopically light carbon may have been derived from the oxidation of organic matter such as petroleum and/or kerogen (Zhu et al. 2011) during thermochemical sulfate reduction. As suggested in the paragenetic sequence (Figure 8), the association of hydrocarbon to later mineralization is likely one of the latest diagenetic events and correlates with calcite cement (C7) A25, which represents the lightest carbon calcite. Warm brines associated with MVT mineralization cause thermal maturation of organic matter in host rocks producing hydrocarbon gases such as CH_4 , C_2H_6 , and C_3H_8 (Anderson 1991). If these gases are trapped, they can provide a reductant for sulfate in the fluid such as dissolved anhydrite or gypsum and, furthermore, produce H_2S for metal sulfide precipitation. This process may explain the interruption

of calcite zones by thin sulfide precipitates. Lighter carbon values may also be explained by meteoric diagenetic fluids where $\delta^{13}\text{C}$ values reflect dissolved limestone and dissolved soil gas. Although meteoric calcites commonly have light $\delta^{13}\text{C}$ values, $\delta^{18}\text{O}$ values typically remain constant (Lohmann 1988). The first of these two processes is more plausible to explain the light carbon. However, the increasing values of $\delta^{18}\text{O}$ in the calcite cements remain ambiguous. The $\delta^{18}\text{O}$ possibly is a reflection of the fluid temperature, but fluid inclusion and other studies are required to verify this suggestion. Further, each calcite zone likely reflects pulses of fluid that begin with sulfide precipitation as a result of gas build up in the cavity and the mixing of upwelling fluids. With regards to the two isotopic trends (Figure 19), calcite cements (C3 to C5) A12 to A17 would be one similar sourced fluid, and (C6 to C7) A20 to A25 would be another fluid.

As previously noted, the sulfide precipitation (marcasite and pyrite) sequence is an excellent indicator of compositional changes within the diagenetic fluid with respect to pH. Further inference may also be made based on the morphology of the sulfide crystal. Experiments run by Murowchick and Barnes (1987) showed that the crystal morphology of pyrite directly reflects the temperature and degree of supersaturation of the solution from which the crystals precipitate. They found that low degrees of supersaturation at temperatures below 250°C produced acicular pyrite crystals that presumably grew via a screw-dislocation growth mechanism. Higher degrees of supersaturation resulted in the development of cubic, octahedral, and pyritohedral forms. As a result, the sulfide zones have been used as another tool to delineate compositional and temporal changes of burial diagenetic fluid flow. The most notable change in pyrite morphology is sulfide zone (S4) A18. A18 (S4) is primarily composed of stacked and skewed or stretched pyrite octahedrons (S-4, Figure 17). A18 is located just below calcite zone (C5), which has a very high CL intensity (Figure 13), suggesting a relatively high Mn/Fe ratio or relatively low abundance of quenching elements such as Fe^{2+} . Murowchick and Barnes (1987) hypothesized that fluid tempera-

ture and degree of supersaturation is reflected by pyrite morphology. Furthermore, the CL character implies that the diagenetic fluid was undersaturated or at low supersaturation with respect to iron, resulting in sulfide crystal precipitation, which might explain the stacked appearance of the octahedrons (Figure 17 S-4) and suggest acicular growth in sulfide zone (S6) A21 (S-6, S-6', Figure 15).

A18 is one of numerous small sulfide cements (S3 through S6) A16, A18, A19, and A21 precipitated along concentric growth planes of calcite cements (C4 through C6) A15, A17, and A20. These sulfide cements (S3 through S6) may be interpreted as very weak pulses of metal (iron) carrying slightly acidic brine moving up the fractures and mixing with formation waters to precipitate the sulfides. The lack of dissolution suggests that these pulses are very weak but sufficient to change the pH slightly and precipitate marcasite. A component of mixing of two fluids is suggested based on the descending $^{87}\text{Sr}/^{86}\text{Sr}$ ratios corresponding to the calcite cements in the cavity as a function of time. Furthermore, the repetitive sequences of diagenetic events and the overall decrease of diagenesis as a function of time favors a weakening influx of deeper subsurface fluids mixing with formation waters. An alternative hypothesis of mixing, as mentioned previously, is that a warm, acidic, sulfate- and metal-bearing solution heated and dissolved the carbonate host rocks, resulting in kerogen maturation, generation of methane, and reduction of sulfate by thermochemical sulfate reduction, H_2S buildup, and the precipitation of sulfides (Anderson 2008).

In summary, the solution cavity and subsequent mineralized cements formed by pulses of at least two different fluids that decreased in intensity over time and likely mixed with other subsurface formation waters or gas buildup within the cavity. Isotopic signatures of early cavity cements reflect deep basin brines, whereas later cements reflect the influence of shallower formation water that may have been in contact with evaporite minerals, such as those in the overlying Silurian carbonates (Fisher et al. 1988, Winter et al. 1995). It is likely

that the progressively weaker pulses of upwelling migrating fluid may directly reflect regional stress regimes and/or subsidence dynamics imposed on the basin fluid dynamics and may further be a product of major tectonic events such as the Taconic, Acadian, and/or Alleghenian orogenies (Garven et al. 1993, Coakley et al. 1994, Winter et al. 1995). To further test this hypothesis, the study of paragenetic events of proposed MVT deposits at Conco Mine should be compared with other paragenetic studies of regional MVT deposits and MVT-bearing host rock.

Regional Paragenetic Comparisons

The results of this study suggest that solution structures and mineral deposits at Conco Mine are MVT deposits. Mineral deposits at Conco generally follow the general characteristics of MVT deposits (Sverjensky 1986), occurring

principally in limestone and dolostone that form a thin sedimentary cover over Precambrian igneous basement rock; they are strata bound and epigenetic; they consist of massive sulfide and calcite deposits; there is no known association with igneous rocks; they exist in a region of mild deformation expressed by a gently sloping basin, slight faulting, and fractured bedrock; the minerals are present at shallow depths on the flank of a basin; and along with massive solution cavities, there is other evidence for dissolution expressed by collapse and brecciation of the bedrock and etching of crystals. This new discovery of MVT deposits at Conco Mine may provide new clues to fluid flow mechanics and the subsequent diagenesis of bedrock. Therefore, it is necessary to compare paragenetic relationships of structures and mineralization at Conco with other regional MVT deposits and similar age host rock in order to understand paragenetic differences unique to the study

area and similarities relating paleofluid flow to other regional diagenetic events. Paragenetic sequences established for the UMV (Figure 19), Ordovician limestone deposited along the eastern Wisconsin Arch in the western Michigan Basin (Figure 20), and Trenton hydrocarbon reservoirs in the southern and southeastern Michigan Basin (Figure 21) are reviewed and compared with the paragenetic sequence established for Conco Mine. Common paragenetic events between localities are reported (Figure 22) and discussed in the context of diagenetic fluids.

Upper Mississippi Valley Zinc-Lead District

The UMV mineral deposits are hosted primarily by Ordovician carbonates on the northwest flank of the Illinois Basin (Figure 1) located in northwestern Illinois, southwestern Wisconsin, and eastern Iowa on a structural high defined by

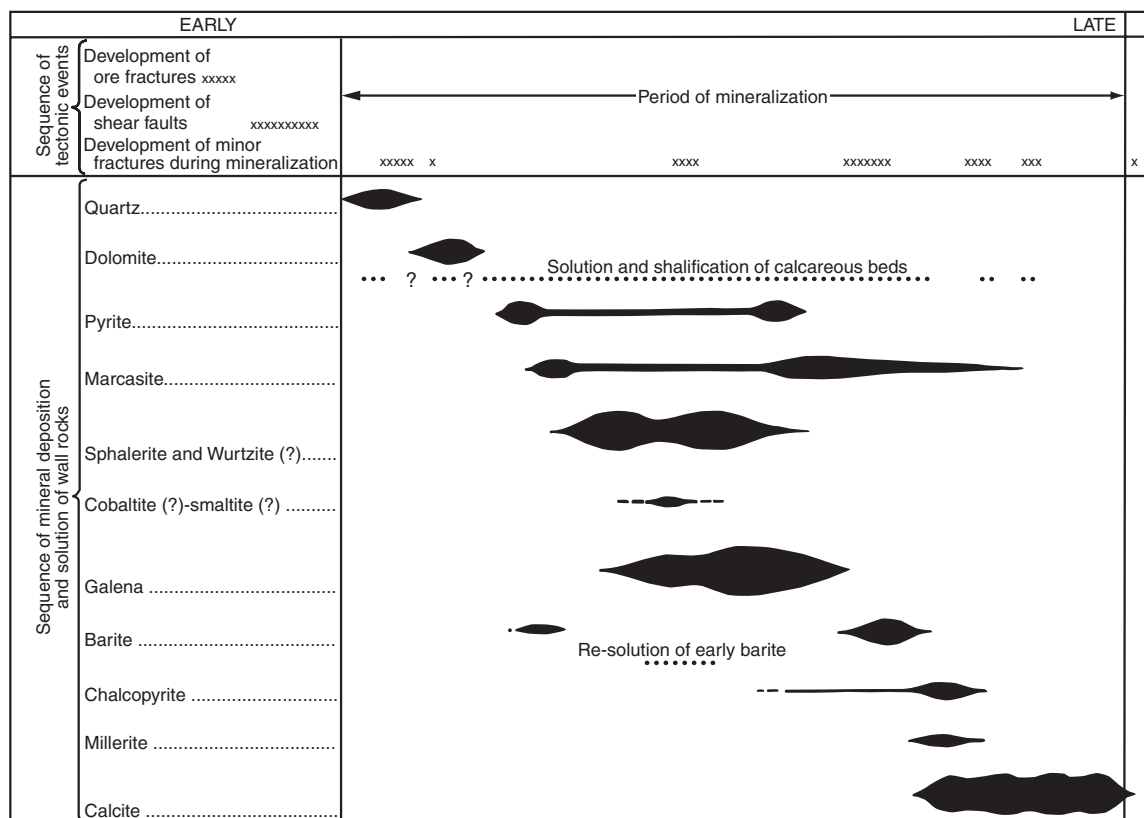


Figure 20 Paragenetic sequence of the Upper Mississippi Valley Zinc-Lead District primary ore deposition (Heyl et al. 1959). All dolomitization is paragenetically earlier than primary ore mineral deposits except for quartz, and pyrite is earlier than marcasite. Four stages of calcite are noted.

the Mississippi River, Wisconsin Arch, and Kankakee Arch, which separate the Illinois Basin from the Forrest City Basin to the west and the Michigan Basin to the northeast (Figure 1). The seminal manuscript on the geology of the UMV by Heyl et al. (1959) is reviewed here to compare the geology and paragenesis of those sites with that of Conco Mine. The total area of the district is approximately 10,369 km². The vast majority of primary mineral deposits are found within dolomitic limestone. Island-like areas of unreplaced limestone have been noted at UMV; however, most of the Galena Group is dolomitized. The UMV is famous for zinc- and lead-based minerals, especially sphalerite and galena. Iron sulfides are also primary minerals at UMV and are paragenetically associated with lead and zinc sulfides, which is not always the case; it should be noted that iron sulfides are highly variable at MVT deposits (Marie et al. 2001). In general, iron sulfide deposits at UMV, along with other continental MVT deposits known for significant amounts of iron sulfides, are paragenetically earlier than lead and zinc minerals (Marie et al. 2001) but are typically deposited throughout the duration of the lead and zinc mineralization.

Heyl et al. (1959) describe the paragenesis of UMV with a focus on tectonic events and the deposition of primary minerals (Figure 20). At UMV, fractures are the main control of the ore body and are proposed as being early deformation events predating mineralization. Dissolution along fractures and the formation of solution structures is proposed to follow shortly thereafter. One of the main differences at UMV relative to Conco Mine is the presence of a wide range of MVT minerals, but specifically zinc and lead sulfides. However, a small amount of sphalerite was found in one of the cavities at Conco during this study, suggesting more may yet be discovered. At UMV, the first ore stage mineral to precipitate in the paragenetic sequence is quartz, which is dominant as a replacement in the host rock in the form of chert and is predominately found in close relation to fracture zones. Dolomite is the second stage of mineralization at UMV. Dolomite is deposited within vugs and fractures that crosscut an earlier, widespread regional

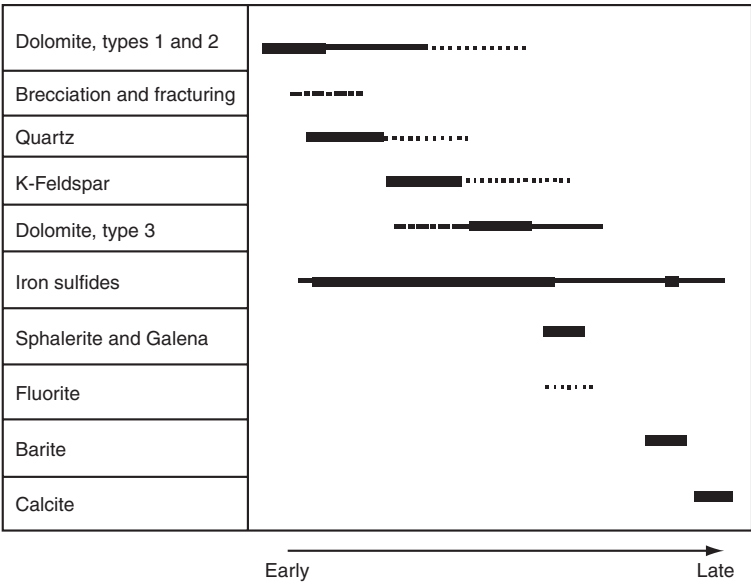


Figure 21 Paragenetic sequence of the general mineralization observed in the Sinnipee Group (Galena-Platteville Groups) in eastern Wisconsin on the western margin of the Michigan Basin (Luczaj 2006). All iron sulfides, calcite, and the final stage of dolomitization are precipitated post fracturing and brecciation.

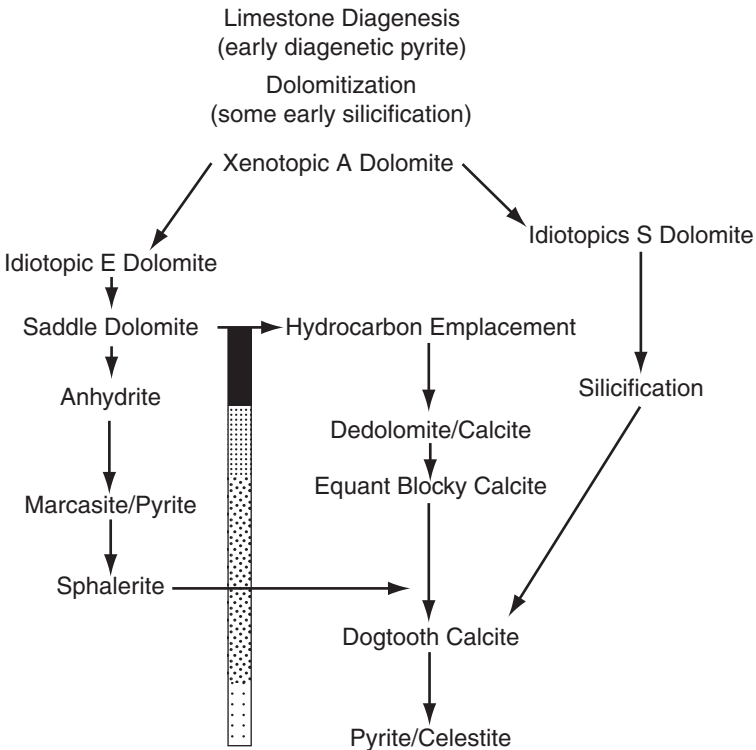


Figure 22 Paragenetic sequence of the Trenton Group (Galena Group) in southwestern Ontario on the southeastern margin of the Michigan Basin (Colquhoun 1991). The vertical bar represents observed hydrocarbons (dark indicates 100% of the time; stippled indicates 25% of the time).

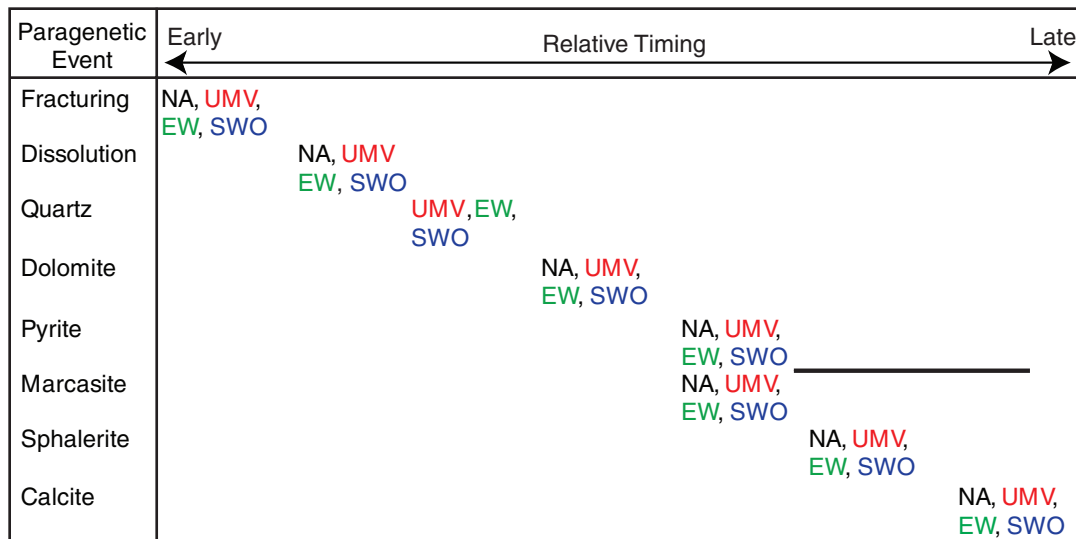


Figure 23 Comparison of paragenetic events from the Upper Mississippi Valley Zinc-Lead District (UMV; comparison 1, Figure 1), eastern Wisconsin (EW; comparison 2, Figure 1) in the western Michigan Basin, and southwestern Ontario (SWO; comparison 3, Figure 1) in the southeastern Michigan Basin, all relative to the study area (Figure 1) at the Conco Mine (NA). Only paragenetic events from Conco are represented if one or more of the study locations include a similar event. However, a quartz cementation event is included because all of the study locations included this event except Conco Mine. Marcasite and pyrite are cementation events that begin relatively early and end late.

matrix dolomitization. Dolomites are described as fine-grained and pink. They are restricted to fractures and ore zones and predate all sulfides. A second dissolution event is described that dissolves limestone and dolomites along fractures, creating very porous media for the transport of fluid and subsequent sulfide precipitation. Heyl et al. (1959) notes that dissolving solutions did not alter the paragenetically earlier dolomitized limestone as much as adjacent less dolomitized limestone of the same beds. The main period of dissolution is suggested to be after dolomitization. Barite and pyrite follow the main dissolution event. Barite is brief and not widespread. The pyrite is described as lining solution cavities and cementing interstices in host rock and partially dissolved dolomites. Pyrite mineralization is suggested to have occurred over a long period of time but to have ended before calcite precipitation. Early pyrite likely formed octahedral crystal habits, whereas later pyrite formed more cubic habits. Marcasite precipitation is thought to have formed directly after pyrite and is separated by a sharp contact between the pyrite. Marcasite continues to pre-

cipitate through most of the remaining ore deposition and is proposed to have increased in deposition after sphalerite deposition, gradually decreased thereafter, and ended after all other sulfides were emplaced. Other primary minerals to be deposited during marcasite deposition include barite, sphalerite, galena, chalcopyrite, millerite, and suspected wurtzite, cobaltite, and safflorite. However, sphalerite is the most abundant mineral found at UMV. Calcite is the final stage of mineralization and includes four substages. Marcasite is deposited in the first two stages of calcite precipitation. Early calcite is cloudy and colored; as deposition continued, calcite became increasingly clear to colorless, with fewer impurities. Substages of calcite deposition are recognized by three early scalenohedral habits followed by a final rhombohedral habit. All substages can be further identified by episodes of dissolution or slight etching of the crystal face and marcasite zones in the first two stages (Heyl et al. 1959).

Relative to the paragenesis of the solution cavity researched at Conco (Figure 8), UMV has clear paragenetic

differences and many interesting similarities that may correlate (Figure 23). One major difference is the lack of hydrocarbons at UMV. At Conco Mine, hydrocarbons altered to bitumen have been noted as inclusions in dolomitized burrows (A5) above the solution cavity and at the top of the Wise Lake Formation, heavily staining fractures and vugs. Briefly mentioned at UMV is oil staining associated with the dark, organic-rich Guttenberg Dolomite (lower Galena Group, Figure 3); however, there is no mention of hydrocarbons throughout the primary ore mineral paragenesis. Quartz cement and silicification is another paragenetic difference. Quartz cement along fractures and silicification of the host rock are prevalent at UMV. The only occurrence of quartz in the solution cavity at Conco noted in this study is primary depositional rounded quartz grains in the host rock; however, chert has been noted in the Wise Lake Formation in drill core examined from the South Mine.

Heyl et al. (1959) proposed a later-stage dolomitization at UMV that postdates quartz precipitation. This dolomitiza-

tion event is likely related to the main dissolution event. A similar stage dolomite (A10) is proposed at Conco Mine that may be closely related to the main cavity-forming dissolution event (A9). At both locations, dolomites are slightly dissolved and replaced by the first sulfide cement. However, UMV later-stage dolomite fits a description of saddle dolomite where dissolution-related dolomites at Conco are described as more planar dolomites (Figure 10d). Pyrite is proposed as the first sulfide to precipitate at UMV with marcasite following shortly after. At Conco Mine, marcasite is the first sulfide to precipitate with pyrite co-genetically precipitating afterward. Based on the results of pyrite and marcasite precipitation studies (Murowchick and Barnes 1986; Schoonen and Barnes 1991a, 1991b, 1991c), it makes more sense for marcasite precipitation followed by pyrite precipitation to follow a dissolution event if both events are genetically related to the same fluid. In this case, an acidic fluid evolving to less acidic fluid is expected. In the UMV, based on the paragenetic ordering, a fluid would be expected that is becoming increasingly more acidic. However, with the lack of dissolution constraints during sulfide precipitation at UMV, it is difficult to track the pH changes and individual sulfide precipitation of the fluids.

A major similarity between the two locations, in addition to co-genetic precipitation of marcasite and pyrite, includes multiple stages of calcite precipitation. However, only marcasite is described to be co-genetic with the first two stages of calcite at UMV. At Conco, marcasite and pyrite are paragenetically related to cavity calcite cements (C3 through C6). Calcite appears to be the last paragenetic event at both sites. An interesting similarity between the sites is the association of two dissolution events with marcasite and calcite precipitation. At UMV, the first and second calcite precipitation events or stages end with a dissolution event. Marcasite precipitation continues through the first dissolution event and ends at the second dissolution event, suggesting a paragenetic relationship. At Conco Mine, the first two dissolution events A9 and A13 are related to marcasite precipitation

and subsequent calcite precipitation. This similarity is suggestive of similar late-stage diagenetic environments. Interesting also are the crystal habits of each calcite stage documented at UMV. The first three stages are noted as scalenohedral habits and the last stage as rhombohedral. It was previously noted that smaller cavities in Conco typically contain only scalenohedron calcite crystals, suggesting that these are paragenetically early relative to UMV paragenesis. Other larger cavities included combined scalenohedral-rhombohedral habits where both scalenohedrons with later stage rhombohedral growth and rhombohedral with later scalenohedral growth are exhibited. These findings further suggest relatively similar diagenetic environments between UMV and Conco Mine, but further examination is needed of other cavities at Conco.

There were pre-existing structural boundaries between the two deposits before mineral deposition. The Cambrian to Devonian age uplift of the Wisconsin Arch (Paull and Paull 1977, Nelson 1995) predates a Permian age of ore emplacement at UMV, based on Rb-Sr dating of sphalerite (Brannon et al. 1992). Based on fluid inclusion studies of sphalerite from UMV (McLimmers 1977) and calculated thermal requirements (Bethke 1985, Rowan and Goldhaber 1996), UMV ore-depositing fluids likely migrated from south to north and had a recharge zone in the Appalachian-Ouachita fold belt (Bethke and Marshak 1990). Furthermore, Permian Ar-Ar age dates of hornblende and biotite in igneous dikes and breccias associated with the fluorspar district in southern Illinois (Snee and Hayes 1992) correlate with age dates at UMV, indicating that igneous activity in southern Illinois may have been a heat source for northward migrating fluids. Further evidence that fluid flowed from the south to north is provided by the abundance of MVT minerals along the Mississippi Valley Arch, such as chalcopyrite, galena, barite, and sphalerite in eastern Iowa (Garvin 1995) and the decreasing concentrations of fluorine in drill core from the fluorspar district northwest up to UMV (Goldhaber et al. 1994). Hypothetically, fluid flowing from deep in the Illinois Basin northeastward

toward Conco during the late Paleozoic would have been bound to the south by pre-existing structural highs such as the Kankakee Arch and uplifted strata on the southern side of the Sandwich Fault. The MVT trace minerals deposits are found on the steeply dipping northeast flank of the Illinois Basin in Indiana (Shaffer 1981) but terminate quickly before reaching the Kankakee Arch, further suggesting structural constraints on fluid flow. However, on the north side of the Kankakee Arch in Indiana there are multiple occurrences of MVT mineralization, especially in northwestern Indiana (Brock and Slater 1978, Shaffer 1981), indicating that fluids were being transported along the northern flank of the Kankakee Arch. Possible fluid sources include the Michigan Basin or the Eastern Appalachian Basin.

Western Michigan Basin (Eastern Wisconsin)

Conco Mine is located on the far southwest flank of the Michigan Basin. Previous research has suggested a fluid flow out of the Michigan Basin (Colquhoun 1991, Coniglio et al. 1994, Yoo et al. 2000, Luczaj 2006) to explain late-stage dolomitization and MVT mineralization. Luczaj (2006) suggested that Ordovician carbonates are nearly to completely dolomitized east of the Wisconsin Arch in Wisconsin and provided evidence for a strong hydrothermal dolomite signature, and tracing MVT mineralization along the western flank of the Michigan Basin. Thus, we compared the mineral paragenesis in the Sinipee Group (Galena Group equivalent) in eastern Wisconsin (Figure 1) with that at Conco.

A paragenetic sequence of the general mineralization within the Sinipee Group in eastern Wisconsin (Figure 20) begins with two stages of dolomitization; the first is described as a planar dolomite composing most of the rock, and the latter is described as a finer dolomite that typically replaces cloudy cores of the first dolomite. Brecciation and fracturing occur during the first and second dolomitization events. Undifferentiated iron sulfide precipitation is associated with dolomitization events 1 through 3. Quartz cementation during the first two dolomitization

events marks an increase in iron sulfide precipitation. Dolomitization event 3 occurs near the end of the major iron sulfide precipitation and at the beginning of trace sphalerite and galena precipitation. Iron sulfide precipitation continues in trace amounts, increases slightly during brief barite precipitation, and decreases during calcite precipitation. Calcite is the last mineral proposed to precipitate in the Sinnipee Group (Galena Group) in eastern Wisconsin. No hydrocarbons were observed in this study.

Similarities occur in the mineral paragenesis of the Sinnipee Group in eastern Wisconsin and at Conco and may be correlated (Figure 22). Both sites appear to have undergone three dolomitization events, and at least one of those was intimately related to sulfide or MVT mineralization. Luczaj (2006) noted that marcasite either replaced or co-precipitated with dolomite 1, suggesting marcasite is the first iron sulfide to precipitate similar to the occurrence at Conco. Also, iron sulfides and calcite are the last minerals to precipitate. Both paragenetic studies found that sulfide minerals are preferentially precipitated along fractures and joints in the bedrock, suggesting an element of structural control on fluid transport. However, dissolution events distinguishing compositional changes in fluids and constraining the timing of events at Conco Mine are absent in the paragenetic sequence of eastern Wisconsin. Also differing from Conco is the occurrence of quartz, k-feldspar, galena, fluorite, and barite, which are found throughout eastern Wisconsin. This finding may be related to scale differences between the two studies and, therefore, the scale of the paragenetic sequence.

Luczaj (2006) suggests fluid flow out of the Michigan Basin based on multiple lines of evidence, but does not rule out the Precambrian basement as a fluid and heat source. Middle Paleozoic ages yielded for k-silicate mineralization are consistent in eastern Wisconsin and into the Michigan Basin. This finding differs from the later Paleozoic ages that have been suggested for ore deposition at UMW. Luczaj (2006) also found that dolomitization decreases west of the Wisconsin Arch; the arch probably acted as

a barrier for westward migrating fluids. The Wisconsin Arch and Kankakee Arch would have acted equally as barriers in northeastern Illinois for southward and westward migrating fluids. However, these lines of evidence do not rule out an Appalachian Basin fluid source.

Southeastern Michigan Basin (Michigan and Ontario)

Diagenetic alteration of the Trenton (Galena Group) in the southern and southeastern Michigan Basin has been recognized as a factor in the creation of hydrocarbon reservoirs. The paragenetic sequence of hydrocarbon reservoirs on the southeastern flank of the Michigan Basin in Ontario is reviewed (Figure 21) and compared with that at Conco (Figure 22). Also, the famous Albion-Scipio Trend in the southern Michigan Basin (Figure 1) is reviewed briefly for contextual diagenetic comparison with the cavities at Conco. Both locations provide evidence for late-stage paleofluid flow and MVT mineralization.

A paragenetic sequence of hydrocarbon reservoirs in the Trenton Group (Galena Group) on the southeast flank of the Michigan Basin (Figure 21) was compiled to compare and relate petrographic textures to hydrocarbon generation (Colquhoun 1991). Little evidence of the original rock type exists due to pervasive dolomitization, but overall the rock is referred to as a wackestone with thin beds of interbedded grainstones (Colquhoun 1991). An early diagenetic pyrite is proposed to predate dolomitization.

Widespread dolomitization is the next event described. All dolomite descriptions are based on the classification scheme of Gregg and Sibley (1983). Xenotopic-A (anhedral) dolomite is proposed to be the paragenetically earliest event of dolomitization. However, xenotopic-A crystals are described as being the most pervasive dolomite adjacent to fractures, which are not included in the paragenetic sequence. Idiotopic-S (subhedral) dolomite and idiotopic-E (euhedral) dolomite are suggested as later dolomitization events in the paragenetic sequence. Bitumen is found most commonly around idiotopic-S dolomites

staining the crystal faces or along crystal boundaries. Idiotopic-E dolomites are also found enclosing xenotopic-A dolomites and are commonly stained with bitumen. Saddle dolomites are proposed as the next dolomite to precipitate, followed by hydrocarbon emplacement.

Silicification is thought to occur after idiotopic-S dolomites; however, paragenetic ordering of silicification in relation to saddle dolomites is unclear. Saddle dolomites are found exclusively lining fractures and vugs. Saddle dolomites are described as zoned and contain dedolomite replacements zones of blocky calcite, suggesting calcite precipitation as the next event within fractures and vugs. Anhydrite likely precipitates over saddle dolomites; however, the paragenetic relationship of dedolomite replacement calcite is unclear. Pyrite and marcasite are described as the next cementation events lining fractures and cavities. Sphalerite is deposited over pyrite cement, placing it as a paragenetically later event; however, blocky calcite is described as fracture fill over pyrite cement in some cases. Calcite scalenohedrons (dogtooth spar) are suggested as always being found in association with sphalerite precipitation and occurring paragenetically later. Celestite is proposed as the last cement; however, the paragenetic sequence suggests a relationship with late-stage pyrite. There is no description of this pyrite.

Colquhoun (1991) suggests that dolomitization of the Trenton in Ontario occurred in a fluid-dominated environment in which hydrothermal fluids were emerging from deeper in the basin. These hydrothermal fluids are proposed to be responsible for the generation of hydrocarbons. Relative to Conco, idiotopic-S dolomite in southwestern Ontario is most closely described as burrow dolomitization A6. Idiotopic-E, xenotopic-A, or saddle dolomite may be related to dolomitization events A5 or A10 at Conco; however, this is unclear. Relationships between the two paragenetic sequences (Figure 22) include calcite and sulfide cementation events within fractures with the exception of sulfate precipitates (anhydrite and celestite). Blocky calcite is proposed as the first later-stage cementation event, but the exact paragenetic timing between

the calcite, marcasite, and pyrite is unclear. In southwestern Ontario, blocky calcite precipitates first, and later more euhedral calcite crystals precipitate, much like the findings at Conco Mine. Also, precipitation of sphalerite after pyrite at southwestern Ontario is not included in the paragenesis of the cavity studied at Conco Mine, but has been noted in another nearby cavity at Conco. Slight structural and paragenetic similarities occur between the reservoirs studied by Colquhoun (1991) in the southeastern Michigan Basin and results for Conco. Other prolific hydrocarbon reservoirs in the southern Michigan Basin, such as the Albion-Scipio Trend, are famous for cavernous porosity thought to be caused by fracture or fault focused hydrothermal fluids. The diagenesis of the Albion-Scipio Trend is compared with diagenesis at Conco Mine for regional and diagenetic context.

The Albion-Scipio field is one of the most well-known fracture-controlled hydrocarbon reservoirs in the Michigan Basin. Unfortunately, a paragenetic sequence of Albion-Scipio was not found to enable a paragenetic comparison with that of Conco. Instead, structural and mineralogical similarities are noted herein. Like Conco, Albion-Scipio is located on a shallow synclinal structural sag with prevalent northwest-southeast-trending fractures. Porosity within the hydrocarbon trap is diagenetic in origin and is developed solely in areas of pervasive dolomitization along and above fractures (Hurley and Budros 1991). Dolomitized zones are commonly vuggy and cavernous. Saddle dolomites line vugs and fractures (Radke and Mathis 1980), and other minerals such as anhydrite, pyrite, calcite, and trace amounts of fluorite, sphalerite, and barite have been noted as late-stage cementation events (Shaw 1975, Budai and Wilson 1986, Hurley and Budros 1991). Collapse breccias are common and associated with caverns (Hurley and Budros 1991) or solution cavities. Thin shaly clay beds are also common within the reservoir rock and have previously been thought to be of volcanic origin (Wilson et al. 1985, Harrison et al. 1986, Dehass and Jones 1988). However, spectral gamma-ray tests show no gamma-ray emission

contribution from uranium or thorium, as would be expected from bentonites (Fertl 1983). Gamma-ray emissions resulted solely from potassium, suggesting that if they were from bentonites, the bentonites were originally potassium-rich (Hurley and Budros 1991) and severely altered to illite. Dolomite zones commonly develop near or beneath shale, clay, or bentonite layers at Albion-Scipio (Hurley and Budros 1991), suggesting slight facies control on fluid migration. Among all of the interesting characteristics at Albion-Scipio, the caverns are of greatest interest due to the enormous porosity enhancement of the reservoir and the ability of the caverns to host hydrocarbons. Caverns have been recorded by bit drops when drilling and have been recorded up to 19 m in Albion-Scipio (Smith 2006). Some studies related cavern formation to karst processes (DeHaas and Jones 1988). However, Hurley and Budros (1991) outlined evidence against karst processes, further supporting fracture-controlled solution structure formation. Overall, the structural, stratigraphic, and mineralogical parallels between Albion-Scipio and Conco are fascinating and may be analogous in nature; however, a high-resolution paragenetic sequence needs to be completed and compared before an association can be made.

CONCLUSION

At Conco Mine, the discovery of meter-scale solution cavities lined with tens-of-centimeter-scale sulfide-zoned calcite cements in the Ordovician age Wise Lake Formation are indicative of localized diagenetic events caused by the transport of subsurface diagenetic waters out of midcontinent sedimentary basins. Structural, sedimentological, and geochemical analyses based on a paragenetic sequence of one of these massive solution cavities and mineralization indicate that the solution cavities and minerals within them formed when deep basin diagenetic fluids migrated through regional permeable beds and eventually through localized northwest-trending fractures, causing fracture- and facies-focused dissolution below impermeable boundaries. On the basis of a high-resolution paragenetic sequence (Figure 8) of the diagenetic

events comprising the cavity and mineral cements, a repetitive sequence of diagenetic events is recognized and interpreted as a reflection of the timing and compositional change of the diagenetic waters, and, furthermore, multiple fluidization events or pulses of fluids flowing through the fractures. This repetitive sequence more or less consists of carbonate mineral dissolution, marcasite precipitation, epitaxial pyrite precipitation, and finally calcite precipitation. The PL and CL petrographic evidence suggests that these events within a sequence are genetically related and that they precipitated from the same fluid that was compositionally changing as a function of time.

To further characterize these sequences, cavity calcite cementation events were analyzed for $^{87}\text{Sr}/^{86}\text{Sr}$, $\delta^{13}\text{C}$, and $\delta^{18}\text{O}$ (Table 2). The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for early cavity calcite cements record a fluid that is radiogenic (0.71015 ± 0.00002) and interpreted as deep basin brine expelled to the basin margins. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios become less radiogenic (0.70980 ± 0.00002 and 0.70898 ± 0.00002) in later, younger cavity cements and are interpreted as an influx of formation water as deep basin brine migration slows. $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values for calcites support this notion of two differently sources fluids. Also, light carbon in the calcites suggests that the fluids were warm and capable of thermally maturing bedrock as they passed through, producing hydrocarbon gases, leading to H_2S buildup and sulfide precipitation. The $\delta^{18}\text{O}$ values may reflect temperatures of the fluids and, if so, suggest pulses of fluids are cooling over time. Furthermore, the latest and youngest cavity calcite cement records high concentrations of Na and Sr relative to older calcite cements (Table 2). Elevated Na and Sr concentrations coupled with the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio (0.70898 ± 0.00002) are interpreted as diagenetic fluids that interacted with evaporite deposits in the overlying Silurian bedrock (Figure 3) (Fisher et al. 1988, Winter et al. 1995). Overall, the late-stage diagenetic events forming solution cavities and massive calcite and sulfide deposits record multiple fluidization events and regional fluid transport through sedimentary basins. These events probably reflect regional

stress regimes or subsidence dynamics imposed by major tectonic events such as the Taconic, Acadian, and Alleghenian orogenies (e.g., Garven et al. 1993, Coakley et al. 1994, Winter et al. 1995).

The paragenetic sequence reconstructed for solution cavities at the Conco Mine was compared with other regional MVT deposits and MVT mineral-bearing host rock. Similarities in mineral paragenesis between all locations suggest that solution cavity-forming and mineral-precipitating diagenetic waters are likely related to a common regional system of paleofluid flow. Among all the localities compared, the paragenetic sequence of the solution cavity and subsequent mineralization at Conco resembles the paragenetic sequence of primary mineralization events at the UMV. However, the geographic location and structural boundaries cannot rule out the Michigan or Appalachian Basin as a fluid source. Gangue mineralization at the UMV should be analyzed and compared with mineralization at the Conco Mine and other surrounding mines to interpret and re-examine the source of mineralizing fluids at the UMV. The results of this study imply that other such MVT deposits and cavernous porosity could exist throughout the midcontinent. The paragenesis at Conco Mine may be applied as a tool to predict regional paleofluid flow and assist in future mineral and hydrocarbon exploration. Exploration should focus on areas with similar structural geology (synclinal features and fractured bedrock), sedimentology, and stratigraphy (partially dolomitized limestone, burrowing, and interbedded bentonites). Relating these geologic features to regional and localized paragenetic studies such as at Conco Mine may improve mineral and hydrocarbon exploration efforts.

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APPENDIX

X-ray diffraction analyses from sulfide zone S1 (A11) through S7 (A23).

