Abstract

Recognition and understanding of the important role of sulfur redox processes in developing karst has grown over the last 25 years with the discovery of remarkable sulfur-rich caves worldwide and advances in geomicrobiology. Recent work has shown that microbes interact with hydrocarbons, calcium sulfate bedrock, magmatic fluids, and sulfide ore minerals to reduce gypsum/anhydrite to calcite, produce hydrogen sulfide and sulfuric acid, convert limestone to gypsum, increase porosity in carbonate bedrocks, precipitate massive sulfur, and deposit Mississippi Valley-Type (MVT) ores. These processes are most active in the shallow phreatic and vadose-phreatic subsurface, where transitions between aerobic and anaerobic conditions exist.
6.4.1 Introduction

Recognition and understanding of the role of sulfur redox processes in developing karst has moved into prominence over the last 25 years. The discovery of remarkable sulfur-rich cavities worldwide, several with robust chemoautotrophic (organisms that derive energy from chemical reactions instead of sunlight) ecosystems, prompted a surge in attention to the role of sulfur in karst development (Serbu et al., 1994; Galdenzi and Menichetti, 1995; Hose and Pisarowicz, 1999; Gusinski et al., 2003). Parallel with the growing interest and acceptance of microbe’s role in geomorphology, karst geomorphologists now include knowledge of sulfur redox cycling (changing molecular combinations through oxidation and reduction processes) and microbial functions in their toolbox.

Sulfur-bearing fluids in actively forming karst terrains have been attributed to four sources. Sulfidic waters in Sistema Zacatón are derived from a nearby volcanic/magmatic terrain (Gary and Sharp, 2006). Jagnow (1979) and Morehouse (1968) identified oxidation of pyrite by infiltrating meteoric water as the source of the sulfuric acid that dissolved caves in New Mexico and Iowa, USA, respectively. Bacterially mediated SO$_4^{2-}$ reduction of seawater takes place near the base of the freshwater-seawater mixing zone in Bahamian blue holes, and it enhances dissolution according to Bottrell et al. (1991). Reduction of sulfate in nearby calcium sulfate evaporite beds supplies the sulfidic groundwater in the lower levels of the Frasassi Cave System (Galdenzi and Maruoka, 2003). Some karst terrains may have multiple mixed sources of sulfidic fluids (Hose and Pisarowicz, 1999; Spilde et al., 2004).

6.4.2 Redox Cycling of Sulfur

Redox reactions (oxidation and reduction) of sulfur in groundwater results in a variety of sulfur species that interact with carbonate and sulfate minerals. Sulfuric acid dissolves carbonate and replaces limestone with gypsum, which remains in solution except in arid environments or until the solution becomes supersaturated. Change in the environmental conditions of the groundwater will convert limestone to gypsum. The conversion from limestone to gypsum results in a two-fold volume expansion (and vice versa when gypsum alters to limestone), changes in the solubility of the strata, and nonphotosynthetic energy used by microbes that “fix” (grow) ferromagnesium and other diagenetic minerals. All of these processes contribute to the development of karst in carbonates and calcium sulfate bedrocks, generally leaving distinctive features.

6.4.2.1 Sulfur Oxidation Processes

Meteoric waters (rain and snowmelt) flowing along the surface or infiltrating shallow depths of the Earth’s crust oxidize iron sulfide minerals (pyrite and marcasite) along their paths, releasing H$^+$ and lowering the pH of the water:

$$\text{FeS}_2 + 3.5\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + 2\text{SO}_4^{2-} + 2\text{H}^+$$

The Fe$^{2+}$ ion will further oxidize and hydrolyze to form ferric hydroxide, further generating H$^+$:

$$\text{Fe}^{2+} + 0.25\text{O}_2 + 2.5\text{H}_2\text{O} \rightarrow \text{Fe(OH)}_3 + 2\text{H}^+$$

On exposure of these waters to calcite, the carbonate will readily dissolve. Oxidation of one mole of pyrite can potentially dissolve four moles of calcite:

$$\text{FeS}_2 + 4\text{CaCO}_3 + 3.75\text{O}_2 + 3.5\text{H}_2\text{O} \rightarrow \text{Fe(OH)}_3 + 4\text{Ca}^{2+} + 4\text{HCO}_3^- + 2\text{SO}_4^{2-}$$

In vadose settings, gypsum may replace the limestone bedrock through this process. In phreatic settings, the highly soluble calcium and sulfate ions remain in solution, ultimately flowing out of the areas.

6.4.2.2 Sulfur Reduction Processes

Bacterial and thermal sulfate reduction play significant roles in karst processes. Reduction of sulfate rocks by either process requires a source of hydrocarbon compounds (e.g., petroleum or methane) and water in an oxygen-starved environment. The sulfate is reduced to H$_2$S and the carbon oxidizes yielding a bicarbonate ion:

$$\text{CaSO}_4 \rightarrow \text{H}_2\text{S} + \text{Ca}^{2+} + \text{HCO}_3^-$$

As most near-surface and surface Earth environments have abundant oxygen, sulfate reduction mostly takes place in deep subsurface and deep water settings. Thus, flows from artesian or deep phreatic elements in multilevel systems contain higher sulfide and less bicarbonate than shallow and vadose systems (Worthington and Ford, 1995).

Dedolomitization, the conversion of dolomite to calcite, accompanied by dissolution of dolomite and calcium sulfate makes up one form of meteoric calcitization (Back et al., 1983), which does not play a significant role in karst processes. Bacterial and thermal sulfate reduction processes play more significant roles. Both processes require sulfate rocks and a source of hydrocarbons and result in native sulfur and secondary calcite deposits. Bacterial sulfate reduction can take place in a wide range of temperatures (Machel, 1992). Thermal sulfate reduction is an inorganic process that takes place at temperatures as low as 25 °C (Worden and Smalley, 1996). These compatible processes may both contribute to sulfate reduction in a specific area.

In the Delaware Basin of the southwestern USA, about 70 limestone buttes called “castiles” rise above the Ochoan gypsum plains (Figure 1). These calcitized evaporites are associated with methane and bacterial sulfate reduction at depth (Kirkland and Evans, 1976). More recently, more than 1000 occurrences of calcitization within the Castile Formation have been recorded, including extensive calcitized horizons (limestone sheets and varved laminae). The calcitization concentrates in linear trends that are interpreted as an indication of fluid migration along fractures (Stafford et al., 2008). Native sulfur, secondary selenite, and hypogene gypsum caves are associated with calcification clusters. Stafford et al. (2008) regard these assemblages as evidence of calcium sulfate
diagenesis dominated by hypogene (artesian) speleogenesis (cave development).

Bottrell et al. (1991) described bacterial reduction of sulfates near the halocline at the base of the freshwater–saltwater mixing zone in blue holes (submerged cenotes or sinkholes) in the Bahamas. Stoessell et al. (1993) described the halocline in Yucatan, Mexico as a stable, physical boundary trapping hydrogen sulfide that has been stripped from the anoxic saltwater below. The halocline holds the hydrogen sulfide until it oxidizes back to sulfuric acid through interaction with the overlying, oxygenated freshwater and bacterial mediation. This process contributes to focusing limestone dissolution at the halocline level in Yucatan’s cenotes (Smart et al., 1988).

In each case, reduced sulfur migrating up into shallow depth encounters oxygenated environments and reoxidizes, generating sulfuric acid, which aggressively dissolves carbonate terrains, as well as carbonic acid, which also contributes to the dissolution of adjacent carbonate rocks.

\[
\text{H}_2\text{S} + 2\text{O}_2 \rightarrow 2\text{H}^+ + \text{SO}_4^{2-}
\]

(reaction mediated by some sulfur-oxidizing bacteria)

Or,

\[
2\text{H}_2\text{S} + \text{O}_2 \rightarrow 2\text{S} + 2\text{H}_2\text{O}
\]

\[
2\text{S} + 2\text{H}_2\text{O} + 3\text{O}_2 \rightarrow 4\text{H} + 2\text{SO}_4^{2-}
\]

Development of several major caves in the world has been attributed largely to dissolution by sulfuric acid derived from nearby gypsum/anhydrite units. Calcium sulfate reduction within evaporite basins, along with hydrocarbons in the same basins, has been identified as the source of hydrogen sulfide that fed the famous caves of the Guadalupe Mountains, New Mexico and Texas, USA, including Carlsbad Cavern and Lechuguilla Cave (Hill, 1995b; DuChene and Cunningham, 2006), Frasassi caves, central Italy (Galdenzi and Maruoka, 2003), and the Kane Caves, Wyoming, USA (Egemeier, 1981).

6.4.2.3 Role of Microbes

Microbes play an important and critical role in subterranean sulfur cycling (Sarbu et al., 1994). The exact magnitude and role of their contributions to sulfuric acid karst processes is poorly understood but their participation is clear (Barton and Northup, 2007). Boston has demonstrated that some cave-dwelling bacteria in living laboratory cultures can produce elemental sulfur and gypsum (Hose et al., 2000; Boston et al., 2001). Barton and Luiszer (2005) presented evidence that both sulfate reduction and sulfide oxidation occur simultaneously in sulfidic hot springs in Colorado, USA even in the absence of free oxygen. Sulfate reduction in these subterranean springs generates reactive sulfur species such as sulfite, which can interact with water directly to produce sulfuric acid. They suggest that such activity may lead to higher levels of sulfuric acid production and have a regional impact on water chemistry and subsequent speleogenesis of large cave systems.

Sulfur-cycling microbes play an important role in creating and decorating their subterranean karst homes. Evidence of active, biomediated sulfuric acid speleogenesis has been documented for submerged caves in the Bahamas and Yucatan, Mexico (Bottrell et al., 1991; Moore et al., 1992) and for subterranean spring-fed, air-filled caves including Mexico’s Cueva de Villa Luz (Hose et al., 2000). Italy’s Frasassi Cave (Galdenzi and Menichetti, 1995) and Acquasanta Terme caves (Galdenzi et al., 2010), and the USA’s Lower Kane Cave, Wyoming and Cesspool Cave, Virginia (Engel et al., 2001, 2004). Researchers have documented some specific microbial colonies as contributors to carbonate dissolution and karst development (Marcella et al., 1994; Engel et al., 2004; Macalady et al., 2006, 2007; Jones et al., 2008) (Figures 2(a) and 2(b)). In addition to enlarging subterranean cavities, microbial sulfur cycling also produces byproducts of ferromagnesium, sulfur, and gypsum deposits in carbonate caves (Cunningham et al., 1995; Barton and Northup, 2007).

The biological communities in active sulfur karst systems impart isotopic, mineralogic, and lipid signatures that may help identify fossil caves formed by speleogenesis (Hose and Macalady, 2006). Acidic wall biofilms in multiple caves on two continents contain extremely depleted N signatures that may provide a useful biosignature of sulfuric acid-formed caves (Galdenzi and Sarbu, 2000; Stern et al., 2003). Polyak and Güven’s (1996) detailed analysis of sulfur isotopes provided evidence that microbe-mediated, low-temperature, sulfuric acid-bearing waters exposed to clay-rich sediments in Carlsbad Cavern and Lechuguilla Cave, New Mexico, USA converted clay minerals and quartz to alunite \([\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6]\), natroalunite \([\text{NaAl}_3(\text{SO}_4)_2(\text{OH})_6]\), and hydrated halloysite \([\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4]\cdot\text{H}_2\text{O} + \text{SiO}_2\).

Some workers have projected discoveries of the robust sulfur-oxidizing and reducing microbial ecosystems in subsurface karst into models of potential life on other planets, particularly Mars (Boston et al., 1992, 2001). Citing evidence from Mars of relatively high sulfur abundance, an apparent sedimentary basin with high sulfate concentration, near-surface indicators of ice and water, and trace detection of reduced gases (especially methane) possibly derived from subsurface microbial sources Boston et al. (2006) suggested that sulfuric acid speleogenetic systems may be useful as astrobiological...
analogs for hypothetical Mars ecosystems. Other workers have suggested that the diverse bacteria in sulfidic caves may prove useful toward biotechnological and bioremediation applications (Barton and Jurad, 2007; Mulec, 2008).

### 6.4.3 Epigenic Processes

Clastic rocks upstream may provide a source of iron sulfides as well as autogenic pyrite within a carbonate terrain. Lowe et al. (2000) attributed the high permeability of the Lincolnshire Limestone in eastern England to well developed, dissolutionally enlarged fractures developed by pyrite oxidation reactions in epigenic, but ancient (average 5300 years old), waters. Several researchers suggest that epigenic sulfuric acid processes play a significant role in initiating karst conduits, allowing carbonic acid processes to subsequently dominate speleogenesis following establishment of turbulent flow (Krothe and Libra, 1983; Lowe et al., 2000).

Sulfuric-acid charged, allogetic streams flowing from clastic terrains dissolve major cave passages adjacent to the carbonate contact in China (Bottrell, 1993). Jagnow’s (1979) model for the speleogenesis of Queen of the Guadalupe Mine Cave, New Mexico, USA provided a compelling description of sulfuric acid derived from infiltrating, meteoric water that oxidized pyrite and dissolved the carbonate rocks immediately below, resulting in a vertical shaft cave system. Lauritzen (2001) attributed oxidation of sulfides in insoluble beds along contacts with underlying marble as the corrosive agent that formed small caves in Norway’s marble karst. Development of Toca da Boa Vista in Brazil has also been attributed to oxidation of autogenic iron sulfides (Auler and Smart, 2003).

Even earlier, in 1968, Morehouse described the epigenic sulfuric acid speleogenesis in dolomite forming Level Crevice Cave, Iowa, USA. Oxidation of massive pyrite and marcasite in the Middle Ordovician Galena Dolomite formed the acid. He proposed that artesian waters charged with sulfuric acid dissolved the incipient cave passages along fractures. Following glacial downcutting through the Maquoketa Shale and exposure of the dolomite, infiltrating water from the surface also oxidized sulfides and continued enlarging fractures to form small caves (Morehouse, 1968). However, White (1988) deemed sulfide-mineral-derived sulfuric acid an unimportant player in the development of most cave systems.

Epigenic sulfuric acid has also contributed to distinctive features in cave systems otherwise dominated by carbonic acid processes. Much has been written on the impacts of sulfuric acid processes in the world’s longest known cave, Mammoth Cave, Kentucky, USA. White and White (1969, 2003) have emphasized the role of crystal expansion and resultant wedging in modifying passages and developing domes. They noted that gypsum replaces calcite on a mole-for-mole basis.

![Figure 2](image)
that results in an approximate twofold volume expansion. As sulfuric acid-laden solutions migrate along bedrock discontinuities in otherwise dry environments (i.e., vadose), the limestone alters to gypsum, mechanically wedges open the joints, faults, and bedding planes, fractures the bedrock, contributes to roof and wall spalling, and leaves piles of rubble on cave passage floors. In addition, gypsum "flowers" and needles have extruded from passage walls and floors (Figure 3). Researchers (Pohl and Born, 1935; Pohl and White, 1986; Palmer and Palmer, 1995) have identified the source of the sulfuric acid as infiltrating, epigenic waters oxidizing pyrite in the strata overlying the cavernous Mississippi limestone.

Anthropomorphic, atmospheric acid precipitation also provides a source of sulfuric acid. Unimpacted rainwater has a pH of 5.6–6.4, but emissions from coal-burning power plants and mining smelters lower the downwind rain pH to 3.5–4.5. This acid precipitation attacks calcite in building materials as well as in natural terrains (Lipfert, 1989; Brimblecombe and Grossi, 2008). The importance of acid precipitation on karst development in carbonate terrains is considered negligible (Ford and Williams, 2007), but the role that karst processes play in protecting forest, river, and lake ecosystems from the detrimental effects of acid rain is large. Carbonates rapidly buffer the acidity in precipitation, raise the pH, and ensure slightly alkaline ground and surface water bodies.

The same principle applies to acid mine drainage sites, where sulfide-rich tailings on the surface lower the pH of waters flowing through and over the tailings. This acidic water can quickly form or enlarge karst features in carbonate rocks (Palmer, 2007). In noncarbonate terrains with acid mine drainage issues, limestone rubble is commonly added along drainage paths to raise the pH. Bottrell (2007) demonstrated that a combination of sulfur and oxygen isotopic measurements yields highly effective discriminators of sulfate sources (i.e., acid mine drainage, or acid rain) to a karst aquifer.

6.4.4 Hypogenic/Artesian Processes

6.4.4.1 Active, Sulfur-Rich Hypogenic Caves

Standard textbook models of cave development (speleogenesis) in carbonate terrains describe processes involving meteoric water infiltrating into or onto the bedrock after picking up carbon dioxide in the air and soil. Limestone (or dolomite) is very slowly dissolved by this dilute carbonic acid over an extensive period of time forming rillen, dolines, caves, and sinkholes. Similarly, meteoric water flowing onto or along fractures in gypsum strata dissolves the bedrock to form equivalent features. Most caves in carbonate and evaporite strata formed through these processes.

However, the last 25 years of speleological research have brought a growing recognition of the role sulfuric acid plays in speleogenesis. The first proposal of speleogenesis by sulfuric acid actions of limestone was made by Principi (1931). Morehouse (1968) provided the first English proposal, describing the epigenic sulfuric acid speleogenesis that formed Level Crevice Cave, Iowa, USA. The concept received little attention, mostly regarded as a novelty, until the mid-1980s, when exploration and research began in several remarkable caves with active, thermal, sulfide-rich water bodies. For example, the Frasassi cave system in Italy, Movile Cave in Romania, and Cueva de Villa Luz (aka Cueva de las Sardinas) in Tabasco, Mexico. Work in these caves, and others added to the list in the following decades (e.g., Kane Caves in Wyoming USA, Sistema Zacatón, Mexico, and Acquasanta Terme in Italy), have advanced our understanding of the importance of sulfur redox processes in the development of many karst systems.

Active sulfidic cave systems contain hypogenic/artesian, subterranean springs. These rising waters are warmer than the ambient cave air and wall rock temperatures, and have elevated CO₂ concentrations in addition to measurable dissolved sulfur. Cooler meteoric water infiltrates from the surface and mixes with the hypogenic waters. Temperature gradients may be significant, leading to powerful thermal convection processes. Upwelling thermal waters meet colder, oxidized, meteoric waters, inducing H₂S oxidation, mixing corrosion, and cooling corrosion (Dublyansky, 2000). These environmental influences of hydrochemical mixing interactions between the phreatic and vadose zones elevated CO₂ and convection/evaporation driven atmospheric circulation with vigorous condensation on walls and ceilings strongly contribute to the morphology of these caves (Palmer, 1991). These conditions also result in common geologic, biological,
and geomicrobiological characteristics that distinguish these cavens from those formed by epigenic caves (Hose and Macalady, 2006).

Sulfuric acid speleogenesis follows a general, three-step process:
1. Early sulfide-rich phreatic phase forming incipient karst conduits;
2. Sulfide-rich vadose-phreatic phase of chemical weathering and mechanical stoping;
3. Sulfide-depleted vadose phase of epigenic speleogenesis.

Sistema Zacatón, Mexico provides an interesting example of a cave system in transition between early, phreatic, and secondary vadose-phreatic phase of sulfuric acid speleogenesis. Deep phreatic shafts (including the 329 + m deep El Zacatón), more than 2 km of ramiform vadose cave passages, broad overland travertine flows, collapse dolines, travertine-filled sinkholes, horizontal phreatic conduits, relict springflow travertine, and rillenkarren characterize this karst system (Gary and Sharp, 2006). Biomats of sulfur-cycling bacteria line the walls of the water-filled sinkholes (“cenotes”) and likely contribute to enlarging these giant pits (Gary, 2002). Gary and Sharp (2006) attribute the sulfur in the system to a nearby volcanic complex.

The vadose-phreatic phase produces many geologic and biological characteristics unique to caves formed in sulfuric and hypogenic mixing environments. The Frasassi and Acquasanta Termé caves in central Italy (Galdenzi and Maruoka, 2003; Galdenzi et al., 2010) and Cueva de Villa Luz, Mexico (Hose et al., 2000) provide excellent examples of caves at this stage of development. Subaerial corrosion and microbial mediation, including mineral deposition, play prominent roles during this stage.

The tertiary phase may destroy most of the evidence linking an ancient cave to a sulfidic origin, particularly after surface erosion breaches and forms an entrance to a cave abandoned by hypogenic waters. Epigenic waters and processes overprint the earlier features and remove or cover most or all evidence of an earlier stage of hypogenic, sulfidic speleogenesis. Thus, the importance of sulfuric acid speleogenesis, particularly in the early stages of cavern development, is difficult to accurately assess. Commonly preserved evidence of previous sulfide-driven speleogenesis includes horizontal levels of large passages connected by vertical rifts, abruptly terminating passages, major passages formed parallel to axial planes, gypsum crusts on walls and ceilings, piles of gypsum sediments on the floor, subterranean rills, and speleosols. These features are best preserved in arid environments like the Guadalupe Mountains of southwestern USA.

6.4.4.3 Oil Field Karst and Sulfur Deposits

The common proximity of petroleum, evaporites, carbonates, caves and karst, degassing hydrogen sulfide, and economic sulfur deposits in sedimentary basins throughout the world (e.g., Delaware Basin in southwest USA, Villahermosa Basin in Mexico, and Carpathian Basin in Ukraine) suggests their genetic interrelationships. Although geologists have long studied the relationship between carbonates, evaporites, and the formation of oil and gas, their connection with karst has only recently received significant attention. Davis (1980) and Egemeier (1981, 1987) were among the first to propose that karst features (including major caves) were formed from H₂S migrating from petroleum in basin sediments into a karst terrain. Later, others began to recognize the complexity of the role of sulfur species in the diagenesis, reservoir porosity, and karst processes of petroleum basins (Hill, 1990, 1995a; DuChene and McLean, 1989). Today, geologists recognize a strong genetic relationship between hydrocarbons, native sulfur deposits, Mississippi-Type ore concentrations, and sulfuric acid karst through a series of sulfur redox reactions (Hill, 1995a).
Oxidation of hydrogen sulfide, as described above, may develop porosity in potential reservoir bedrocks. Alternatively, mixing of saturated solutions with different H2S concentrations, resulting in a mixed, unsaturated solution below the equilibrium curve, may drive dissolution (Palmer, 1991). The first process requires free oxygen and is, thus, limited to shallower depths. The mixing process may take place at greater depths, below the zone of free oxygen. Both processes undoubtedly occur, but Hill (1995b) judged the mixed water model more important than oxidation in developing porosity in deeply buried sediments.

Secondary porosity generated through these means enhances the reservoir capability of carbonate strata to allow fluid transport and to host concentrated petroleum and mineral deposits. Hill (1995a) cited the Yates (southwestern USA), Lisburne (Alaska, USA), and the Middle East’s Kirkuk Fields as examples of major oil reservoirs where sulfuric acid was the likely source of the host rocks’ porosity.

Oxidation of H2S leads to precipitation of elemental sulfur (see previous), which fills karstic voids in carbonate and evaporate terrains. The Culberson Sulfur deposit, west Texas, USA had an estimated 4.6 x 10^7 metric tons of sulfur mined from a karst breccia pipe over 30 years in the late twentieth century (Wallace and Crawford, 1992; Hill, 1995b; Harman, 1998). Klimchouk (1997) provided arguments for a model of large-scale sulfate reduction and development of gypsum/anhydrite karst as a major prerequisite for the formation of epigenetic (nonvolcanic) sulfur deposits. Studying the Pre-Carpathian region of Western Ukraine, he has determined that cave systems in gypsum/anhydrite beds formed by upward flowing (artesian) water, which dissolved sulfate ions. Biogeochemical mechanisms oxidized the sulfate in a low-temperature, diagenetic environment, and precipitated sulfur in karst cavities.

### 6.4.4.4 Metallic Ore Deposits

Sulfuric acid karst processes play important roles in many economically valuable mineral deposits, most prominently lead, zinc, and iron ores. Not only do paleokarst cavities host many of these deposits throughout the world, sulfuric acid processes also contribute to their genesis and result from their weathering. Microbial mediation processes between hydrogen sulfide, sulfuric acid, and metallic sulfides, and vice versa, have also been documented in hypogenic caves (Hose et al., 2000; Southam and Saunders, 2005).

Most lead–zinc ores are sulfides that formed in an anoxic, subsurface environment where dissolved metals bonded with the sulfur in dissolved H2S, which was derived from the reduction of gypsum, anhydrite, petroleum, or other sulfur-rich compounds. The most common lead and zinc minerals are galena (PbS) and sphalerite (ZnS). These sulfide minerals commonly concentrate in the collapse and clastic sediments filling old karst features. Greater porosity in the remnants of earlier cave passages and sinkholes, called “paleokarst”, facilitate metal-bearing fluid transport through the host carbonate stratum. These carbonate strata-bound lead–zinc deposits, often also associated with fluorite and barite, are called Mississippi Valley-Type deposits or MVTs. Major MVTs include the central Mississippi drainage basin in the central USA, Pine Point Mine of the Northwest Territories, Canada (Guilbert and Park, 1986), and Lennard Shelf, Western Australia (Dörling et al., 1998).

The genetic relationship between the speleogenesis of the karst features and the emplacement of the metals remains uncertain. Did fluids derived from sulfate-rich basins move into the carbonate host rocks, oxidize to sulfuric acid, dissolve the caves, and deposit metallic sulfide in those caves? Did the fluid chemistry evolve between the time of speleogenesis and metal deposition? The case connecting the genesis of hypogenic cave development and emplacement of MVT ore deposits has been argued by Furman (1993).

Researchers (Anderson and Macqueen, 1982; Anderson, 1983; Hanor, 1996) suggested that low-temperature H2S brines from igneous sources within zones of compression in the Earth’s crust transported these dissolved metals as chloride complexes. These metal-rich brines mixed with H2S-rich groundwater derived from reduction of sulfate by hydrocarbon compounds. Kesler et al. (2006) have argued that karst plays a key role in the formation of MVT based on evidence from the Precambrian. Very few MVTs formed prior to the Great Oxidation Event (2.4–2.0 Ga). These workers demonstrated that the world’s oldest MVT in the Neoarchean–Paleoproterozoic Transvaal Supergroup, South Africa formed in karstified dolomite under unique, localized conditions.

Hill (1996) envisioned a seven stage development of these related features in the Delaware Basin of the southwestern USA:

- **Stage 1** – Production of H2S from hydrocarbons.
- **Stage 2** – Emplacement of native sulfur deposits.
- **Stage 3** – H2S migrated from basin to reef and helped form MVT sulfide deposits.
- **Stage 4** – Dissolution of cave passages by a sulfuric acid mechanism higher in the reef complex.
- **Stage 5** – Deposition of massive gypsum blocks in the caves.
- **Stage 6** – Deposition of sulfur in the caves.
- **Stage 7** – Oxidation of cave sulfur to cave gypsum.

### 6.4.5 Summary

Recent work has shown that sulfur redox cycling plays an important role in karst development throughout the world. Microbes interact with hydrocarbons, calcium sulfate bedrock, magmatic fluids, and sulfide ore minerals to reduce gypsum/anhydrite to calcite, produce hydrogen sulfide and sulfuric acid, convert gypsum to limestone, precipitate massive sulfur, and deposit MVT ores. These processes are most active in the shallow phreatic and vadose-phreatic surface, where transitions between aerobic and anaerobic conditions exist.

### References


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**Biographical Sketch**

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