Field Trip Guide to Kaolinite Geodes in Hamilton, Illinois, USA

55th Annual Meeting of the Clay Minerals Society
June 10, 2018

TRIP LEADERS:
Jared Freiburg,[1] Georg Grathoff,[2] and Zakaria Lasemi[1]

[1]Illinois State Geological Survey, Prairie Research Institute, Champaign, Illinois
[2]University of Greifswald, Greifswald, Germany

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Front cover: *Kaolinite and quartz in an S-type Keokuk geode. Kaolinite from this geode was analyzed by X-ray diffraction (Figure 39) and scanning electron microscopy (Figure 40). This geode was found in 2017 around Hamilton, Illinois, and measures approximately 7 cm across. Photograph by Ken Vaisvil.*

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ILLINOIS STATE GEOLOGICAL SURVEY
Prairie Research Institute
University of Illinois at Urbana-Champaign
615 E. Peabody Drive
Champaign, Illinois 61820-6918
http://www.isgs.illinois.edu

ILLINOIS
Illinois State Geological Survey
PRAIRIE RESEARCH INSTITUTE

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Figure 1 Field trip points of departure (Champaign, Illinois; green) and arrival (Hamilton, Illinois; red). Image ©2017 Google Earth.

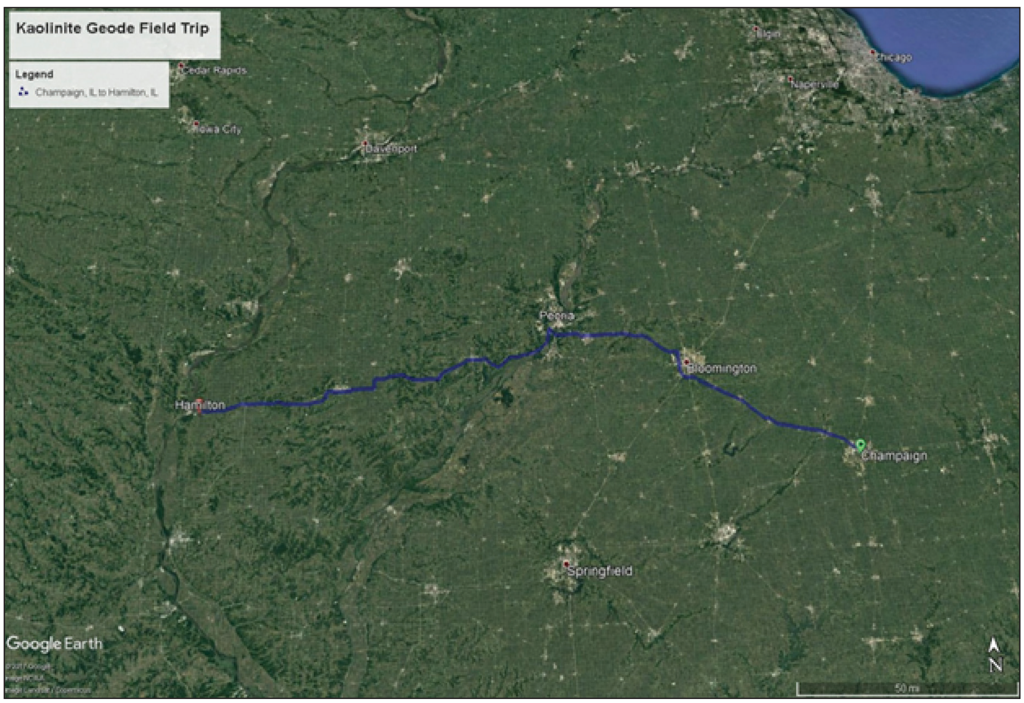

Figure 2 Close up of points of departure (Champaign, Illinois; green) and arrival (Hamilton, Illinois; red). Image ©2017 Google Earth.

LOCATION AND ITINERARY

Welcome to Champaign-Urbana, Illinois, USA, which is located in the Midcontinent of North America approximately 134 mi (215 km) due south of Chicago in east-central Illinois (Figure 1). Today we will be traveling due west to the west-central boundary of Illinois (Figure 2). Our destination is Jacobs Geode Farm (40°22′42.05″N, 91°21′17.11″W) just south of Hamilton, Illinois, and on the east side of the Mississippi River (Figure 3). Jacobs Geode Farm is located on the private property of Gary Jacobs, who operates a pay-to-dig operation. Gary has opened a small quarry into the Warsaw Formation, in which we will be digging for geodes. Please be safe and mindful of your neighbors while digging, have fun, and good luck in your search for highly ordered kaolinite!

Figure 3 Aerial photograph of Hamilton, Illinois, on the east side of the Mississippi River and Keokuk, Iowa, on the west side. Jacobs Geode Farm is just south of Hamilton. Image ©2017 Google Earth.

Table 1 Field trip itinerary

Depart	Location, description	Arrive	Location, description	Mileage
7:00 a.m.	Circle drive, north side of Illini Union, University of Illinois, Champaign	11:00 a.m.	Jacobs Geode Farm, Hamilton, Illinois	177 mi (285 km)
3:00 p.m.	Jacobs Geode Farm, Hamilton, Illinois	7:00 p.m.	Circle drive, north side of Illini Union, University of Illinois, Champaign	177 mi (285 km)

INTRODUCTION

The purpose of this field trip is to collect geodes, with the intent of finding kaolinite within the geodes. During the trip, we will acquaint you with the regional and local geology and discuss the occurrence, origin, and mineralogy of the Keokuk geode. For reference, *geode* is defined as follows in the American Geological Institute's *Glossary of Geology* (Neuendorf et al. 2005):

> A hollow or partially hollow and globular or subspherical body, from 2.5 cm to 30 cm or more in diameter, found in certain limestone beds and rarely in shales; it is characterized by a thin and sometimes incomplete outermost primary layer of dense chalcedony, by a cavity that is partly filled by an inner drusy lining of inward-projecting crystals (often perfectly formed and usually of quartz or calcite and sometimes of barite, celestite, and various sulfides) deposited from solution on the cavity walls, and by evidences of growth by expansion in the cavities of fossils or along fracture surfaces of shells. Unlike a druse, a geode is separable (by weathering) as a discrete nodule or concretion from the rock in which it occurs and its inner crystals are not of the same minerals as those of the enclosing rock. (p. 265)

Theories on the formation of sedimentary geodes have been controversial, and details of their genesis are still debated (Bassler 1908; Van Tuyl 1916; Hayes 1964; Chowns and Elkins 1974; Maliva 1987; Smith 2007; Rakovan 2017).

Hamilton is located in Hancock County in west-central Illinois along the Mississippi River, which acts as the Illinois–Iowa state boundary (Figures 1–3). The region around Hamilton, including Warsaw, Illinois, and Keokuk, Iowa, is referred to as the Keokuk region and is arguably the world's most famous geode locality. Geodes lined with a considerable variation of beautiful minerals are found in the lower part of the Mississippian-age Warsaw Formation. Although disregarded by the locals, one of these beautiful minerals is a highly ordered kaolinite. After all, beauty is in the eye of the beholder!

Keokuk kaolinite has become well known for being a very crystalline kaolinite. John Hayes (1963) was one of the first scientists intrigued by the kaolinite in geodes found in Hamilton, Illinois. Walter Keller, a clay scientist and longtime member of the Clay Minerals Society, continued these studies and used scanning electron microscopy (SEM) to compare Keokuk kaolinite with other kaolinites (e.g., Keller 1976, 1978). He provided samples for several important mineralogical studies (e.g., Bish and Von Dreele 1989; Johnston et al. 1990). This field trip provides the opportunity to collect our own samples.

GEOLOGIC BACKGROUND

The oldest rocks underlying the Keokuk region are Precambrian rocks of the eastern Granite-Rhyolite Province (ca. 1.55–1.35 billion years ago [Ga]). From about 1 to 0.6 Ga, these Precambrian rocks were exposed at the surface. During this time, the rocks were deeply weathered and eroded and formed a barren landscape until the first deposition of Cambrian sediments. This period of erosion or missing time in the rock record from the Precambrian to Cambrian deposition is referred to as the Great Unconformity. A series of tectonic events occurred during the late Precambrian and into the Phanerozoic in areas of Illinois. One of these events was the subsidence of the Illinois Basin and formation of the Paleozoic Sauk, Tippecanoe, Kaskaskia, and Absaroka sequences. The thickest succession of sediments, located within the Illinois Basin depocenter, is in southeastern Illinois and southwestern Indiana. The Keokuk region is located on the far western flank of the Illinois Basin. Pennsylvanian (Absaroka) and upper Mississippian (Kaskaskia) strata were removed by Pleistocene glaciation, exposing lower Mississippian formations such as the geode-bearing Warsaw Formation (Figures 4–7).

The Illinois Basin was a broad, slowly subsiding cratonic embayment that opened southward toward the deep ocean during the Mississippian (Kolata and Nelson 1991). Renewed subsidence during the Late Devonian and the early part of the middle Mississippian resulted in a prolonged episode of sediment starvation after deposition of the organic-rich Upper Devonian–Kinderhookian New Albany Shale (Lane 1978; Lineback 1981). A crinoidal carbonate bank, the Burlington Shelf, developed adjacent to the starved basin at this time. Later, as a result of continued lowering of the relative sea level or renewed tectonic activity in the northern Appalachians, or both, siliciclastic sediment again slowly entered the Illinois Basin from the east and northeast, depositing the Borden Siltstone (Figures 8–11). The transgressive phase of the Borden sequence was characterized by deposition of a predominantly shale unit (lower part of the Warsaw Formation) over the Burlington Shelf to the west and northwest and a very fine grained, siliceous, cherty, and argillaceous limestone of the Fort Payne and its lateral equivalents to the south and east (Lasemi et al. 1998, 2003). This sequence of events was followed by a second phase of sedimentation, which deposited a thick succession of shallow-water carbonate strata, including the upper part of the Ullin as well as the Salem, St. Louis, and Ste. Genevieve Limestones (Lineback and Cluff 1985; Lasemi et al. 1994, 2003).

Warsaw Formation occurs in western and southwestern Illinois, southeastern Iowa, and eastern Missouri. Rocks equivalent in age to the Warsaw are present in western Missouri, Kansas, Nebraska, and throughout the Illinois Basin (Lasemi et al. 1998). Facies analysis and biostratigraphic data suggest that the Warsaw is divisible into an upper and a lower interval (Kammer et al. 1990; Lasemi and Norby 2000). The lower part of the Warsaw is primarily a shale, whereas limestone and, in some areas, dolomite constitute a significant portion of the upper part of the Warsaw.

The separation into lower and upper Warsaw essentially places the thick shales, dolomitic shales, and argillaceous dolomites (often allied with the upper Keokuk) into the lower Warsaw and the poor to moderately sorted, bioclastic grainstones and shaley limestones into the upper Warsaw. This general scenario extends from the type Warsaw area in Hancock County, Illinois, to the St. Louis metropolitan area and appears to extend farther south to the Ste. Genevieve, Missouri, area (Kammer et al. 1990). The paleontologic change that occurs at the contact between the lower and upper Warsaw is chronostratigraphically significant, and Kammer et al. (1990) used this faunal change to mark the Osagean–Meramecian Series boundary.

The upper Warsaw is similar and is equivalent, at least in part, to the upper Ullin Limestone in southern Illinois (Kammer et al. 1990; Lasemi et al. 1998; Lasemi and Norby 2000). The Ullin is a light-colored crinoidal–bryozoan grainstone that ranges in thickness between 150 and 800 ft (45.7 and 243.8 m). Like the upper Ullin Limestone of southern Illinois, the upper Warsaw is primarily a poorly sorted and poorly rounded grainstone dominated by the remains of echinoderms (primarily crinoids) and bryozoans. Poor sorting and poor rounding of grains and the common presence of hummocky cross-stratification in the upper Warsaw carbonates suggest rapid deposition, perhaps in a storm-dominated environment. Similar conditions have been interpreted for deposition of the upper Ullin Limestone to the east in the Illinois Basin (Lasemi et al. 1994, 1998).

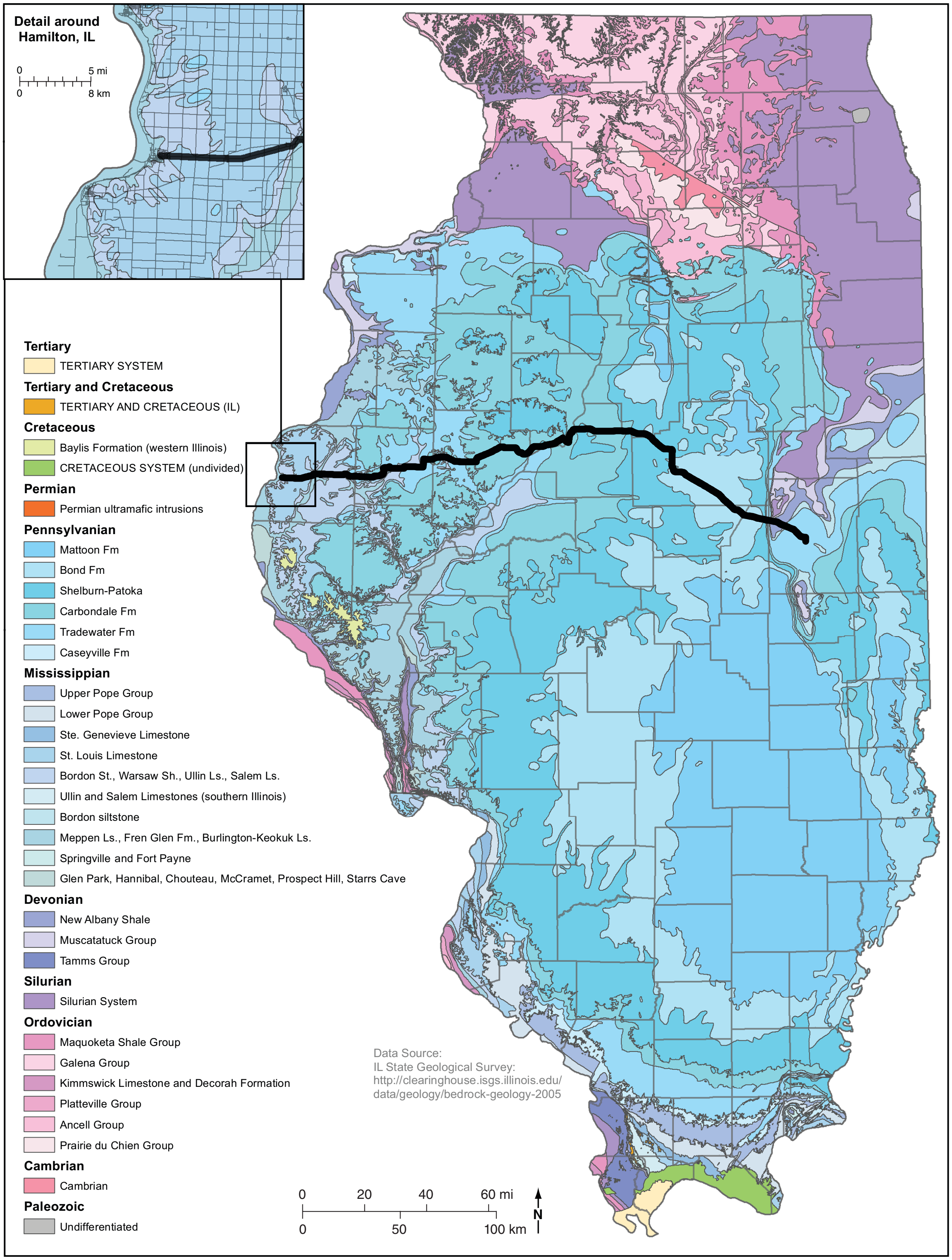

Figure 4 Bedrock geology of Illinois. The black line indicates the anticipated travel route. *Source*: Kolata, D.R., compiler, 2005, Bedrock geology of Illinois: Champaign, Illinois State Geological Survey, Illinois Map 14, 1:500,000. Modified by C. Korose from GIS data available at http:// http://clearinghouse.isgs.illinois.edu/data/geology/bedrock-geology-2005.

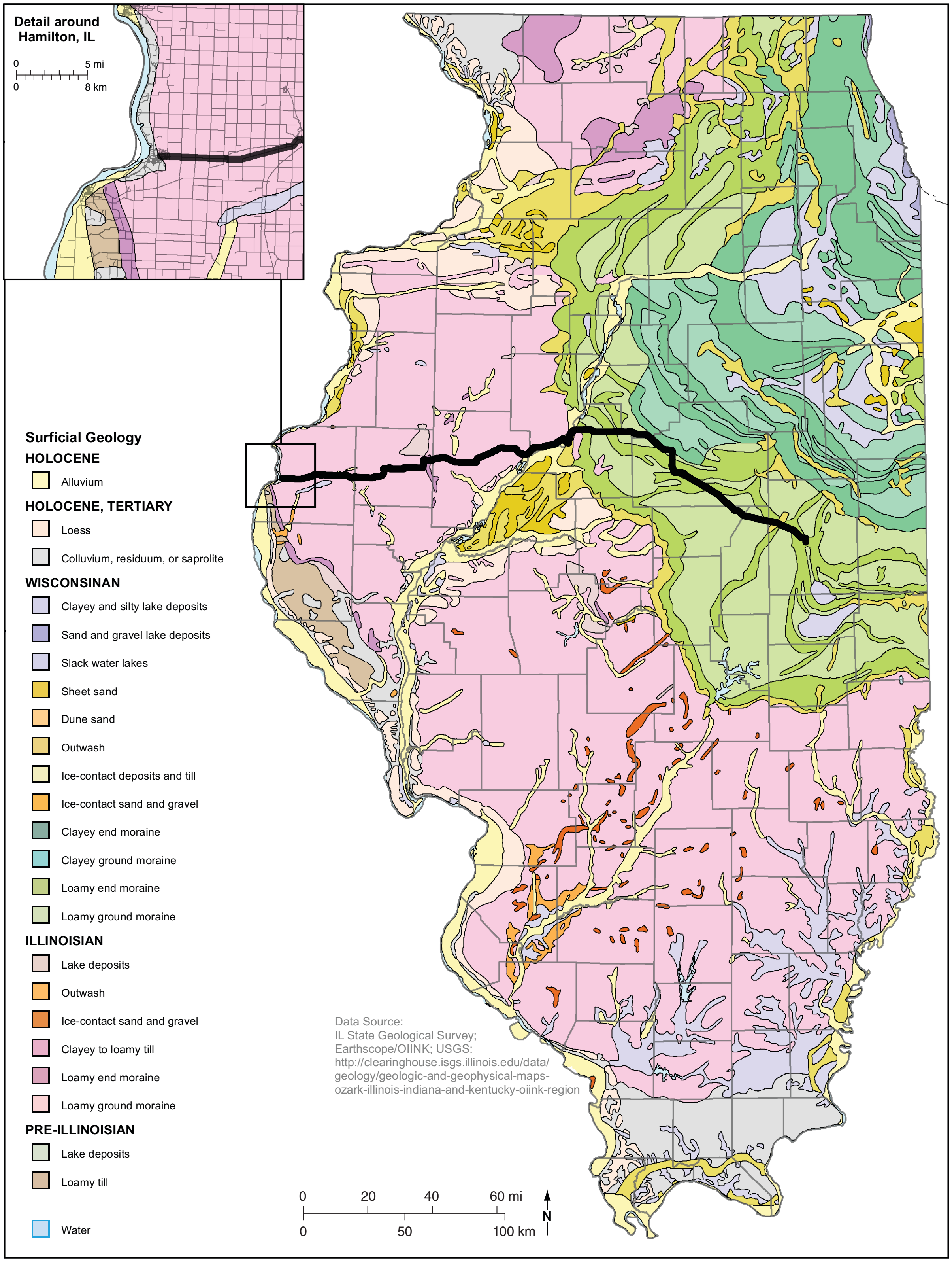

Figure 5 Surficial geology of Illinois. The black line indicates the anticipated travel route. *Source*: Hansel, A.K., and W.H. Johnson, 1996, Wedron and Mason Groups: Lithostratigraphic reclassification of deposits of the Wisconsin Episode, Lake Michigan Lobe area: Champaign, Illinois State Geological Survey, Bulletin 104, 116 p. Modified by C. Korose from GIS data available at http://clearinghouse.isgs.illinois.edu/data/geology/geologic-and-geophysical-maps-ozark-illinois-indiana-and-kentucky-oiink-region.

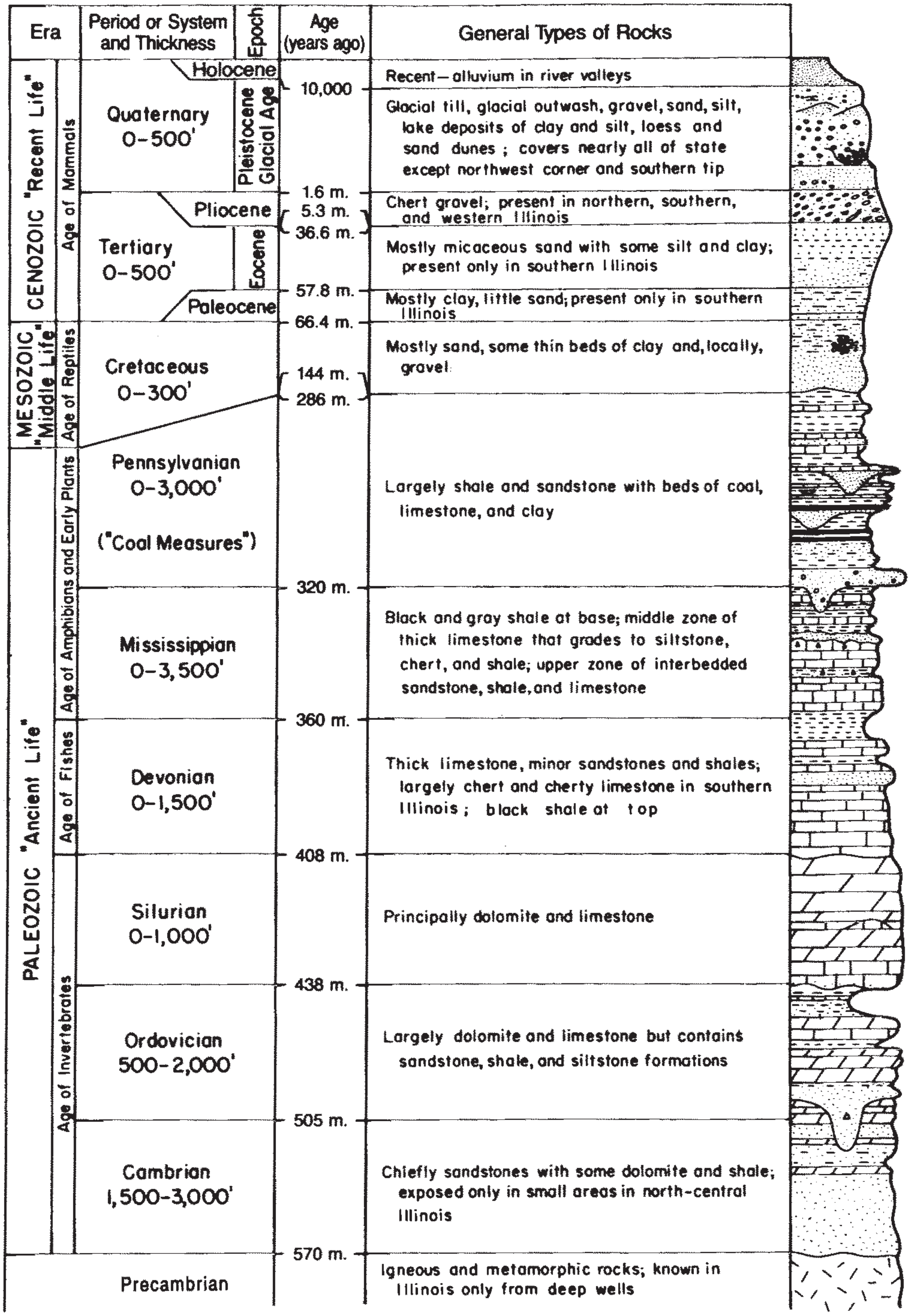

Figure 6 Generalized geologic column showing the succession of rocks in Illinois. *Source*: Frankie, W.T., and R.J. Jacobson, 1998, Guide to the geology of the Hamilton–Warsaw Area, Hancock County, Illinois: Champaign, Illinois State Geological Survey, Field Trip Guidebook 1998A, p. i.

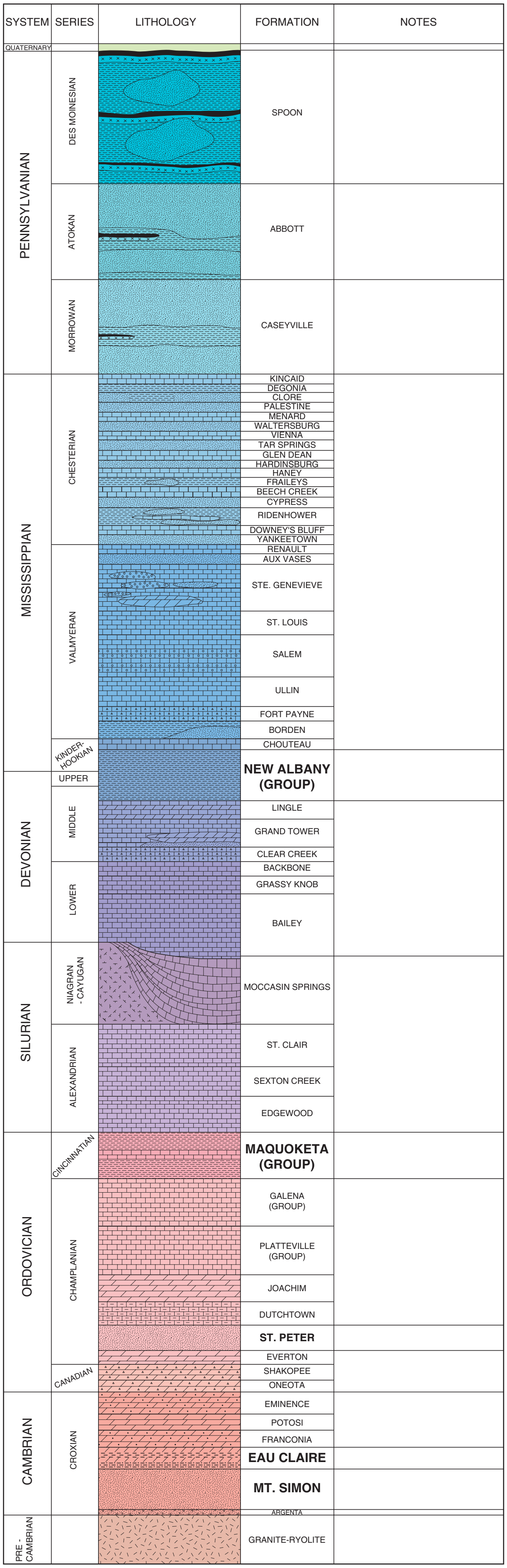

Figure 7 Stratigraphic column of the Illinois Basin. Art by Daniel L. Byers.

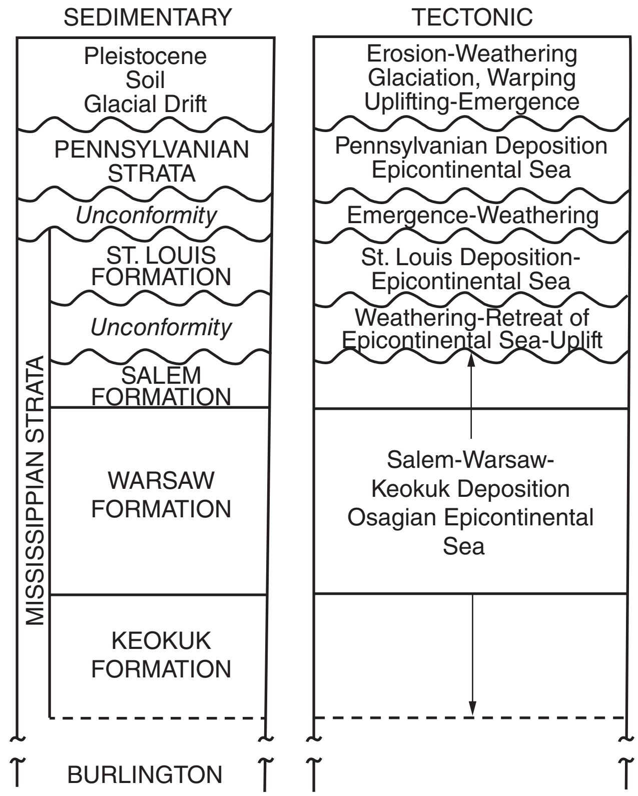

Figure 8 Major sedimentary and tectonic events recognized in the Keokuk–Hamilton area. *Source*: Sinotte, S.R., 1969, T*he Fabulous Keokuk Geodes, Volume I*. Des Moines, Iowa: Wallace-Homestead Co. ©1969 Stephen R. Sinotte. Used by permission of the author.

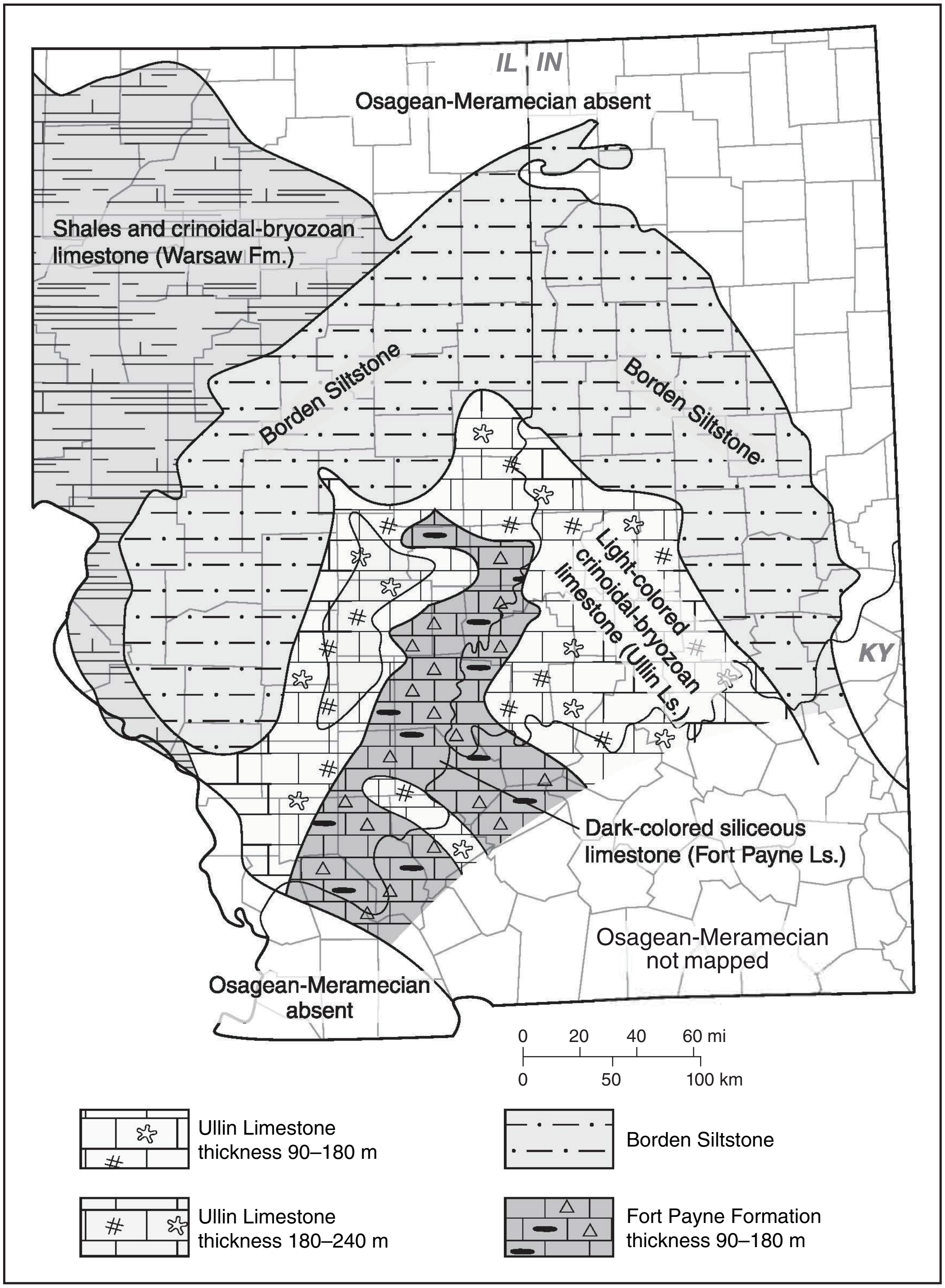

Figure 9 Paleogeography in the Illinois Basin during deposition of the Fort Payne and Ullin Formations, upper part of the Borden Siltstone, and lower Warsaw Formation (modified from Lineback 1966). Note the thick crinoidal–bryozoan carbonates flanking the deep-water Fort Payne Formation. The Fort Payne in the basin is covered by approximately 164 ft (50 m) of the upper Ullin, which is not shown in the figure. The thick Fort Payne represents a preexisting bathymetric depression reflecting deep open ocean to the south. IL, Illinois; IN, Indiana; KY, Kentucky. *Source*: Lasemi, Z., R.D. Norby, J.E. Utgaard, W.F. Ferry, R.J. Cuffey, and G.R. Dever, Jr., 2003, Mississippian carbonate buildups and development of cool-water-like carbonate platforms in the Illinois Basin, Midcontinent U.S.A., *in* W.M. Ahr, P.M. Harris, W.A. Morgan, and I.D. Somerville, eds., Permo-carboniferous carbonate platforms and reefs: Tulsa, Oklahoma, SEPM Special Publication No. 78, and AAPG Memoir 83, p. 69–95. ©2003 University of Illinois Board of Trustees.

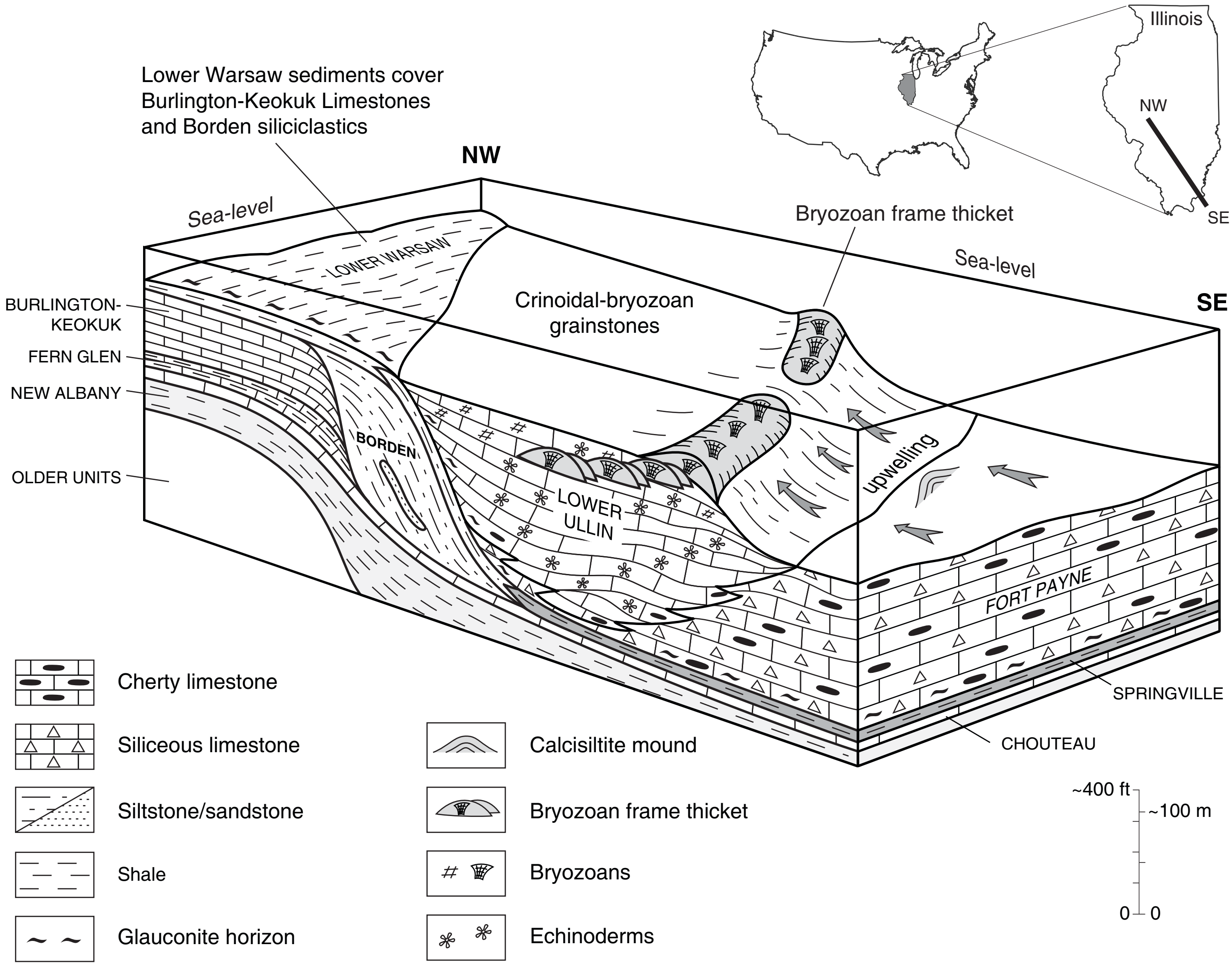

Figure 10 Schematic diagram based on field and subsurface data showing lithologic and stratigraphic relationships between the Fort Payne Formation, the lower Ullin Limestone, and adjacent units, as well as the position of bryozoan frame thickets in the upper Ullin in the Illinois Basin. *Source*: Lasemi, Z., R.D. Norby, J.E. Utgaard, W.F. Ferry, R.J. Cuffey, and G.R. Dever, Jr., 2003, Mississippian carbonate buildups and development of cool-water-like carbonate platforms in the Illinois Basin, Midcontinent U.S.A., *in* W.M. Ahr, P.M. Harris, W.A. Morgan, and I.D. Somerville, eds., Permo-carboniferous carbonate platforms and reefs: Tulsa, Oklahoma, SEPM Special Publication No. 78, and AAPG Memoir 83, p. 69–95. ©2003 University of Illinois Board of Trustees.

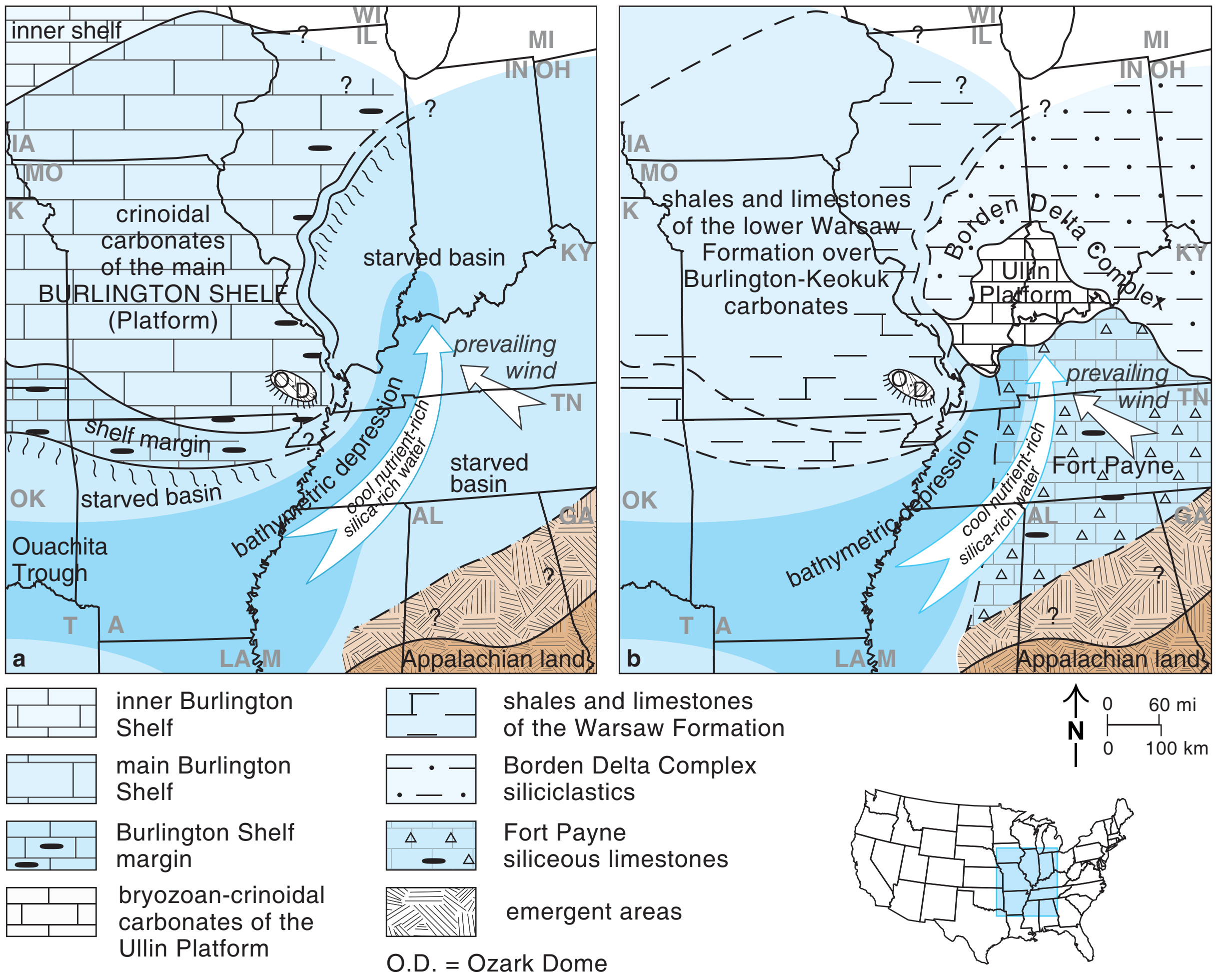

Figure 11 Paleogeographic maps of the U.S. Midcontinent showing the location of the crinoidal Burlington platform and the crinoidal–bryozoan Ullin platform in the Illinois Basin and adjacent regions: (a) Map of the late Osagean (latest Tournaisian) time near the end of Burlington deposition, showing a starved basin adjacent to the Burlington Shelf or platform. (b) Map of the latest Osagean–early Meramecian (early Viséan) time after deposition of the Borden Siltstone, the lower part of the Ullin and the lowermost part of the upper Ullin Limestone, the Fort Payne Formation, and the lower part of the Warsaw Formation. The map shows siliceous and cherty limestones of the Fort Payne on the east and south side of the Fort Payne sea and accumulation of the lower Ullin crinoidal–bryozoan carbonates in the northwest corner of the Fort Payne sea against the Borden Siltstone. IL, Illinois; WI, Wisconsin; IN, Indiana; MI, Michigan; OH, Ohio; KY, Kentucky; TN, Tennessee; GA, Georgia; AL, Alabama; MS, Mississippi; LA, Louisiana; AR, Arkansas; TX, Texas; OK, Oklahoma; KS, Kansas; MO, Missouri; IA, Iowa. Positions of paleogeographic elements modeled after Lineback (1966, 1981); Lane (1978); Craig et al. (1979); Sable and Dever (1990); wind direction after Golonka et al. (1994). *Source*: Lasemi, Z., R.D. Norby, J.E. Utgaard, W.F. Ferry, R.J. Cuffey, and G.R. Dever, Jr., 2003, Mississippian carbonate buildups and development of cool-water-like carbonate platforms in the Illinois Basin, Midcontinent U.S.A., *in* W.M. Ahr, P.M. Harris, W.A. Morgan, and I.D. Somerville, eds., Permo-carboniferous carbonate platforms and reefs: Tulsa, Oklahoma, SEPM Special Publication No. 78, and AAPG Memoir 83, p. 69–95. ©2003 University of Illinois Board of Trustees.

In the Hamilton area, the lower (geode-bearing) part of the Warsaw is predominantly dolomitic mudstone with thin beds of clay-rich to dolomitic limestone (Figures 12 and 13). The upper Warsaw is mostly thick-bedded, shaley limestone composed of fenestrate bryozoans and crinoid fragments. The lower Warsaw can be divided into three lithological units: (1) the basal subunit, (2) the middle fossiliferous limestone, and (3) the upper subunit (Hayes 1961, 1964). Geodes are found in the basal and upper subunits. The basal subunit has an average thickness of 12 ft (3.7 m). It is predominantly composed of indurated blue-gray to brown massive, fine-grained dolomitic mudstone with abundant geodes and no fossils. It also contains a minor facies of fossiliferous limestone with abundant bryozoans and no geodes. Note that geodes form in dolomitic facies and not in calcite facies. Geodes tend to be large in this basal subunit, but smaller geodes are often found as well (Figure 14). The middle fossiliferous limestone often has a mixed carbonate lithology of dolomitic mudstone and fossiliferous limestone with a dominant limestone component. It often contains irregular nodules and anastomosing bands of chert. It is generally approximately 3 ft (0.9 m) thick. The third, or upper, subunit of the lower Warsaw is a blue-gray to brown dolomitic mudstone that is approximately 20 ft (6.1 m) thick. It often contains stringers of partly dolomitized fossiliferous limestone. Geodes are abundant but often small and poorly formed relative to the lower subunit. The following are important observations in the lower Warsaw with respect to the mineralogy:

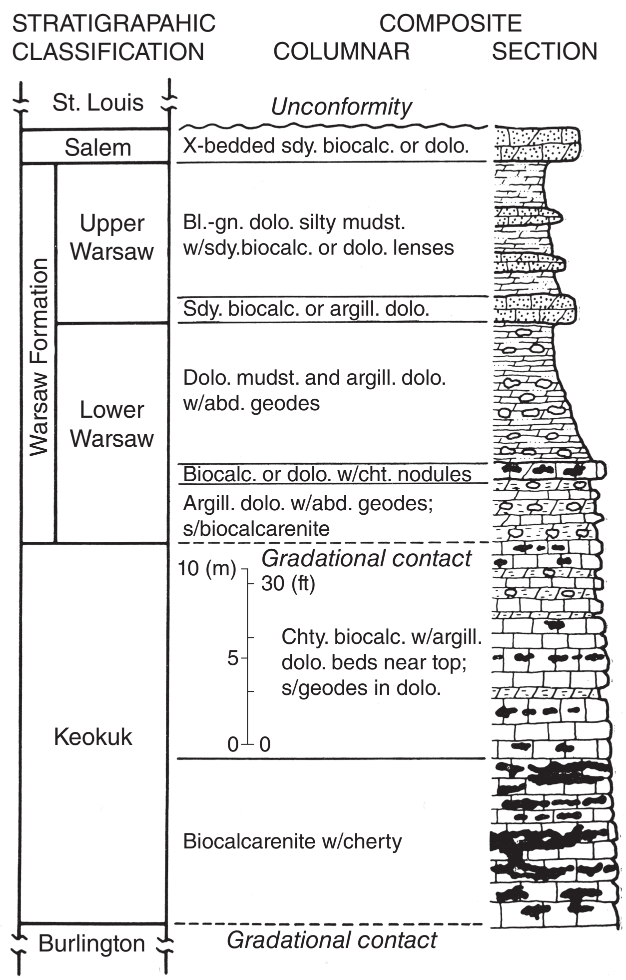

Figure 12 Mississippian rocks in and around the Keokuk–Hamilton area (after Hayes 1964). *Source*: Sinotte, S.R., 1969, *The Fabulous Keokuk Geodes, Volume I*. Des Moines, Iowa: Wallace-Homestead Co. ©1969 Stephen R. Sinotte. Used by permission of the author.

Figure 13 Roger Freiburg digging geodes in the lower Warsaw at Jacobs Geode Farm in Hamilton, Illinois, 2018. Photograph by Jared Freiburg.

Figure 14 Bucket of geodes collected at Jacobs Geode Farm in Hamilton, Illinois, 2018. Note their variable size. Photograph by Jared Freiburg.

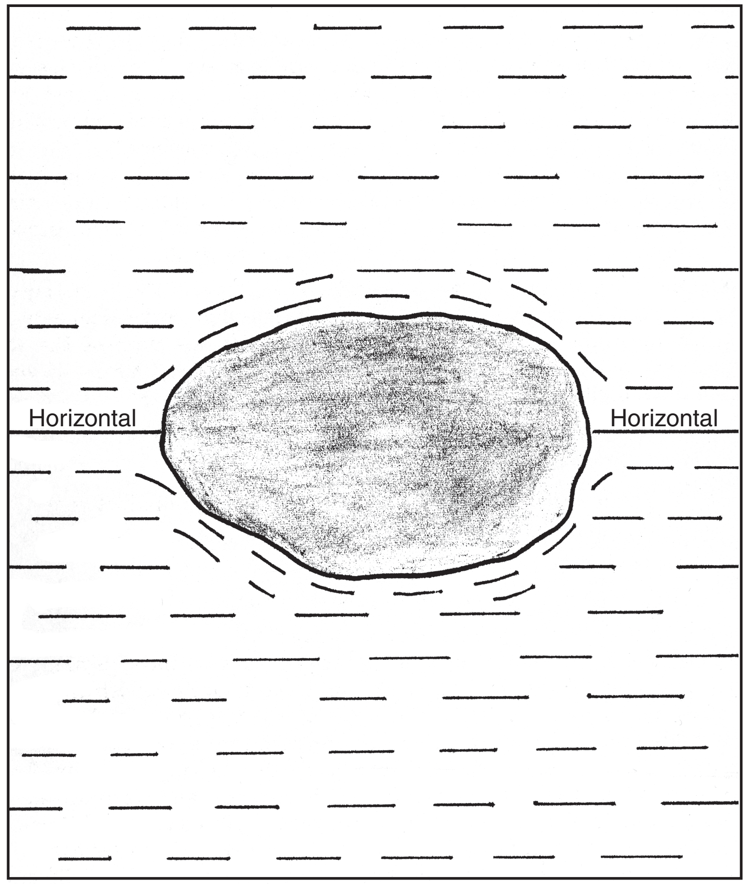

Figure 15 Typical spatial orientation of a geode within bedrock. Notice that the major axis of the geode is parallel to the bedding. *Source*: Sinotte, S.R., 1969, *The Fabulous Keokuk Geodes, Volume I*. Des Moines, Iowa: Wallace-Homestead Co. ©1969 Stephen R. Sinotte. Used by permission of the author.

1. Terrigenous detritus generally increases upward in the lower Warsaw, as does the amount of dolomite in relation to calcite in the fossiliferous limestone.
2. Chlorite and kaolinite are more abundant relative to illite upward.

Geode distribution is a nonrandom phenomenon of the lower Warsaw, where geodes are localized in beds of dolomite and dolomitic mudstone. The distribution of geodes is rather uniform throughout these beds; however, they sometimes exhibit zoning with respect to mineralogy. For example, geodes containing brown iridescent calcite may be restricted or found within a horizon that extends for 100 ft (30.5 m). Geodes often exhibit deformation resulting from compaction and possibly the localized structural warping of strata (Figure 15). Multiple geodes are sometimes cemented together to form a single mass.

GEODE ORIGIN

The first known hypothesis of geode origin was that of Van Tuyl (1912; Figure 16), who stated that geodes formed from calcite concretions on the Mississippian sea floor. Hayes (1961, 1964) confirmed Van Tuyl's (1912) hypothesis and determined how the concretions formed and transformed into geodes.

Calcareous concretions consist of recrystallized sand-sized anhedral calcite crystals with noncarbonate, dolomitic, and silicate impurities much the same as those in the enclosing strata. If not for a chalcedony exterior, the concretion would blend into the strata. The concretions are local phenomena that occurred from the precipitation or accretion of calcite around a pure calcite nucleus. Pyrite is associated with these calcite concretions and is commonly preserved in the shells of geodes. This implies that the conditions in which the concretions formed were devoid of oxygen (i.e., reducing conditions or conditions of negative E_h). Similar conditions exist on the bottoms of seas, where anaerobic bacteria break down dead marine life, producing hydrogen sulfide (H_2S) gas and raising the pH of the water. Hydrogen sulfide combines with dissolved iron to precipitate iron sulfide (FeS). Seawater pH is

Figure 16 F.M. Van Tuyl examining geodes in a lower Warsaw outcrop at the Warsaw Formation type locality in Warsaw, Illinois, circa 1910. *Source*: Sinotte, S.R., 1969, *The Fabulous Keokuk Geodes, Volume I*. Des Moines, Iowa: Wallace-Homestead Co. ©1969 Stephen R. Sinotte. Used by permission of the author.

greater than 8.0, and where organic breakdown is taking place, the pH may increase to more than 9.0. With dissolved calcite in the seawater, the calcite may precipitate out of solution around centers of high pH.

To summarize Hayes's (1961, 1964) diagenetic concretion theory for the origin of geodes, the paragenesis is as follows:

1. Concretions had a diagenetic origin as bioliths forming beneath the water–sediment interface on the floor of the Mississippian sea.
2. Concretions formed under conditions of negative E_h by the precipitation of dissolved calcite over sites of very high pH that resulted from the bacterial decomposition of organic marine life.
3. Early dolomitization and silicification of bedrock occurred, likely concurrently with the initial induration of sediments.
4. During an unconformity between the Salem and St. Louis Formations, acidic groundwater moved through the rock, beginning the epigenetic transformation of the calcite concretions in the lower Warsaw into geodes by dissolving away the calcite core.
5. Variations in the composition of concretions influenced dissolution, giving rise to geodes with different characteristics.
6. During the later Mississippian and Pennsylvanian times, the Warsaw was buried and geode deformation and crushing occurred.

Chowns and Elkins (1974) proposed another viable hypothesis for geode formation similar to that of Hayes (1964) in the sense that geodes arise as pseudomorphs of concretions, except in this case the concretion is anhydrite. In their study of geodes of the Warsaw Formation in Woodbury, Tennessee, they argued that the Keokuk and Woodbury geodes, among others in Indiana, Missouri, and Kentucky, occurred at approximately the same stratigraphic position and share a similar depositional environment. They proposed that a recurrent sabkha facies occurred in a prograding tidal flat–lagoon complex around the margins of the mid-Mississippian–Illinois Embayment. Anhydrite was derived from the evaporation of hypersaline groundwater at the surface of arid supratidal flats. Silicification took place during early diagenesis, with the silica likely being derived from the dissolution of abundant sponge spicules that occurred within the Warsaw Formation.

GEODE TYPE

Three types of geodes have been identified in the lower Warsaw unit based on the cavity shell and the cavity characteristics (Sinotte 1969; Figure 17).

Type S

Type S are siliceous geodes that resemble the calcareous concretion in size and shape. They can be identified by the presence of a recrystallized layer of quartz anhedrons immediately adjacent and interior to a chalcedony shell and the absence of any remnants of original calcite concretion. The quartz/calcite ratio is greater than 50%. Kaolin is common in this geode type, although larger geodes of this type may be completely kaolin free. Type S geodes are common.

Relative Paragenesis

- Chalcedony shell
- Kaolinite
- Sphalerite ⟶ Smithsonite
- Primary pyrite (cubic, octahedral, pyritohedral)
- Quartz anhedrons
- Quartz euhedrons
- Barite
- Calcite
- Dolomite
- Chalcopyrite ⟶ Malachite
- Secondary pyrite (filiform, cubic)
- Marcasite ⟶ Jarosite
- Stilpnosiderite (on brown calcite)
- Goethite ⟶ Hematite
- Pyrolusite
- Selenite

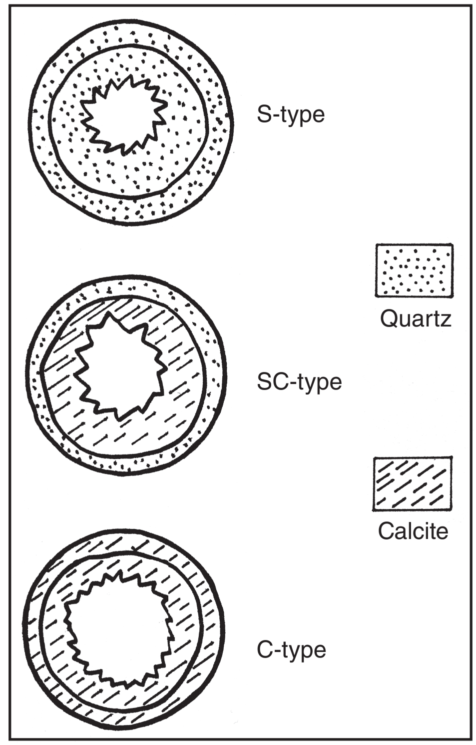

Figure 17 Cross sections through the walls of Keokuk geodes from the lower Warsaw. *Source*: Sinotte, S.R., 1969, *The Fabulous Keokuk Geodes, Volume I*. Des Moines, Iowa: Wallace-Homestead Co. ©1969 Stephen R. Sinotte. Used by permission of the author.

Type C

Type C geodes are similar to Type S except that no quartz is present besides that inherent to the chalcedony shell. Instead of quartz, a recrystallized layer of the original concretion calcite anhedron succeeds the chalcedony shell. This calcite layer is typically lined with a second layer of brown calcite and is commonly fluorescent. Type C geodes contain no kaolinite and likely originated from a very pure calcite concretion. Geodes of Type C are rare.

Relative Paragenesis

- Chalcedony shell
- Primary pyrite (cubic, octahedral, pyritohedral)
- Calcite anhedrons (brown)
- Calcite euhedrons (brown)
- Stilpnosiderite (on brown calcite)
- Dolomite
- Chalcopyrite ⟶ Malachite
- Calcite (white)

Type SC

The presence of brown calcite does not in itself indicate a Type C geode. In the case of the SC-type geode, brown anhedral calcite has been replaced by fine-grained quartz crystals. Subsequent euhedrons of brown or pink calcite are present in varying amounts. The calcite/quartz ratio is greater than 50%. Kaolinite is common, and doubly terminated quartz may be present. Quartz crystallization always predates calcite.

Relative Paragenesis
Chalcedony shell
Kaolinite
Sphalerite ⟶ Smithsonite
Primary pyrite (cubic, octahedral, pyritohedral)
Quartz anhedrons (replacing calcite)
Calcite euhedrons (brown)
Stilpnosiderite
Dolomite
Chalcopyrite
Secondary pyrite (filiform, cubic)
Capillary marcasite and filiform pyrite
Pink calcite
White calcite

MINERALS

Keokuk geodes have previously been noted for containing approximately 20 different minerals (Van Tuyl 1916; Tripp 1959; Hayes 1961, 1963, 1964; Sinotte 1969). Below is a brief description of each mineral.

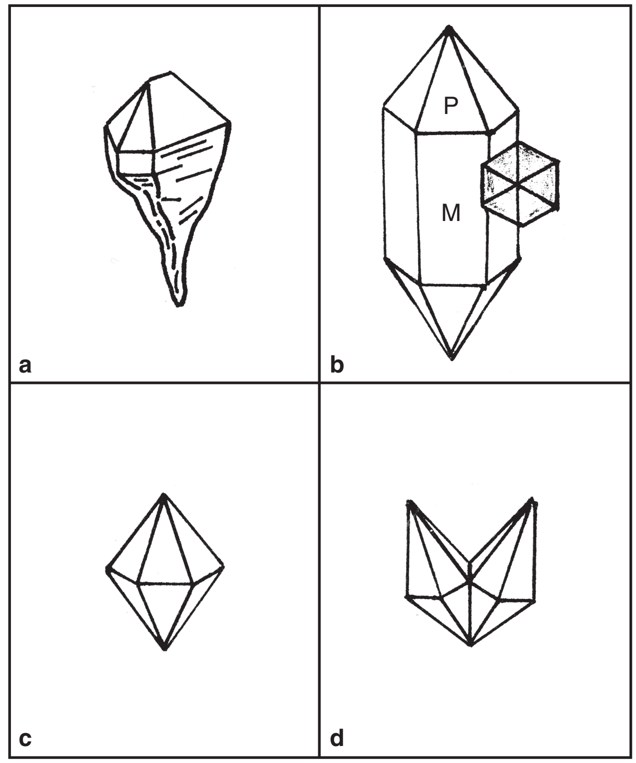

Figure 18 Typical quartz growth habits found in geodes: (a) Distorted crystal from the growth nucleus to a distorted face; (b) prismatic penetration twin with a prism face (m) and pyramidal face (p); (c) dipyramid "dewdrop" prism; and (d) contact twin common in dewdrop geodes. *Source*: Sinotte, S.R., 1969, *The Fabulous Keokuk Geodes, Volume I*. Des Moines, Iowa: Wallace-Homestead Co. ©1969 Stephen R. Sinotte. Used by permission of the author.

Quartz

The most abundant mineral of the Warsaw geodes is quartz. It is the primary constituent of the geode shells and is generally well crystallized. The most common is milky quartz, although translucent quartz is common and can measure up to 4 cm. In rare cases, translucent quartz exhibits zoning with brown inclusions, most likely of iron-bearing minerals. Quartz may exhibit red, brown, yellow, black, and light green discolorations caused by iron staining and iron oxidation states. Quartz exhibits hexagonal prism pyramidal terminations (Figure 18). The pyramid habits are exceptionally brilliant and quite rare. Prism aces are generally highly striated.

One type of geode highly sought after by collectors is the "dewdrop" diamond geode. These S-type geodes lack the prism face of doubly terminated quartz, and the combination of the positive and negative rhombohedrons gives the appearance of nearly geometrically perfect hexagonal dipyramids. The quartz is usually smoky in color and is commonly sprinkled over a background of chalcedony and kaolinite.

Chalcedony

Crystallized quartz is commonly found with chalcedony. Sometimes the geode shells are completely composed of chalcedony, with chalcedony orbs in the interior measuring up to 3 cm (Figure 19). The chalcedony assumes imitative shapes, such as botryoidal knobs, mammillary structures, stalagmitic forms, and encrusting pseudomorphic forms after other minerals, with quartz being the most common. Chalcedony is often color-banded pale blue to blue-gray and is often stained brown to yellow from the oxidation of iron sulfides.

Calcite

Calcite displays more growth habits than any other mineral found in geodes. Calcite scalenohedrons and rhombohedrons measuring up to 7 cm have been found. Early scalenohedrons with later rhombohedral overgrowths are common. Rhombohedrons are sometimes found as a "cap" or "scepter" overgrowth on the scalenohedral termination. Calcite generations are often separated by thin films of marcasite, pyrite, or both (Figures 20–24).

Dolomite

Dolomite occurs as pink to white saddle-shaped crystals measuring up to 1 cm (Figure 25). When dark brown in color, the crystal is assumed to be a weathered ferroan variety of dolomite. Dolomite appears to exhibit a transition from iron-free to ferroan dolomite. Limonite pseudomorphs after dolomite are common.

Barite

In Warsaw geodes, barite always occurs as thin to thick well-crystallized tabular crystals, sometimes forming rosette-like aggregates (Figure 26). The color ranges from blue to white and often exhibits color zoning. Crystals measuring up to 8 cm across can form.

Aragonite

Aragonite forms as white crusts, fibers, and stellate groups of acicular crystals. It is sometimes massive and exhibits a radially fibrous structure. Under long-wave light, aragonite fluoresces and phosphoresces greenish yellow.

Smithsonite

Smithsonite is rare and may be found on altered crystals of sphalerite. It occurs as pale blue to gray botryoidal crystals, yellow to orange microcrystalline granules or earthy powder, yellow to orange rhombohedrons measuring up to 0.5 mm, or a white to peach-colored crust over sphalerite.

Pyrite

Pyrite is most commonly found as cubes measuring up to 1 cm. The cubes are often modified by the octahedron and sometimes pyritohedron (Figures 27–29). Pyrite is often tarnished red to iridescent and sometimes forms capillary crystals that are easily mistaken for millerite. It sometimes forms as oriented growth over capillary marcasite crystals. Pyrite is often found intergrown with or overgrown on quartz, dolomite, ankerite, chalcedony, and calcite.

Marcasite

Marcasite is found as striated single or divergent blades as well as capillary crystals measuring up to 25 mm (Figure 30). It is often replaced by brown limonite pseudomorphs. Twinning is common, with crystals forming chevrons at a 60° angle. Marcasite is most frequently associated with calcite, dolomite, blue

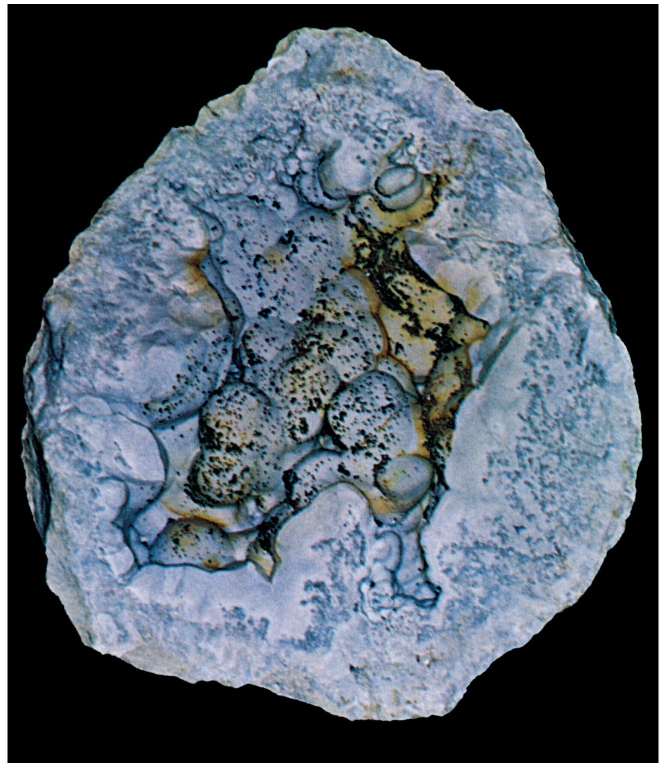

Figure 19 Chalcedony-lined geode with marcasite. Pfeiffer Foundation Museum specimen, Piggott, Arkansas. *Source*: Sinotte, S.R., 1969, *The Fabulous Keokuk Geodes, Volume I*. Des Moines, Iowa: Wallace-Homestead Co. ©1969 Stephen R. Sinotte. Used by permission of the author.

Figure 20 An SC-type geode with quartz, calcite, and capillary marcasite measuring 9 cm in diameter from the lower Warsaw at the Jacobs Geode Mine in Hamilton, Illinois, 2018. Photograph by E. Harrington.

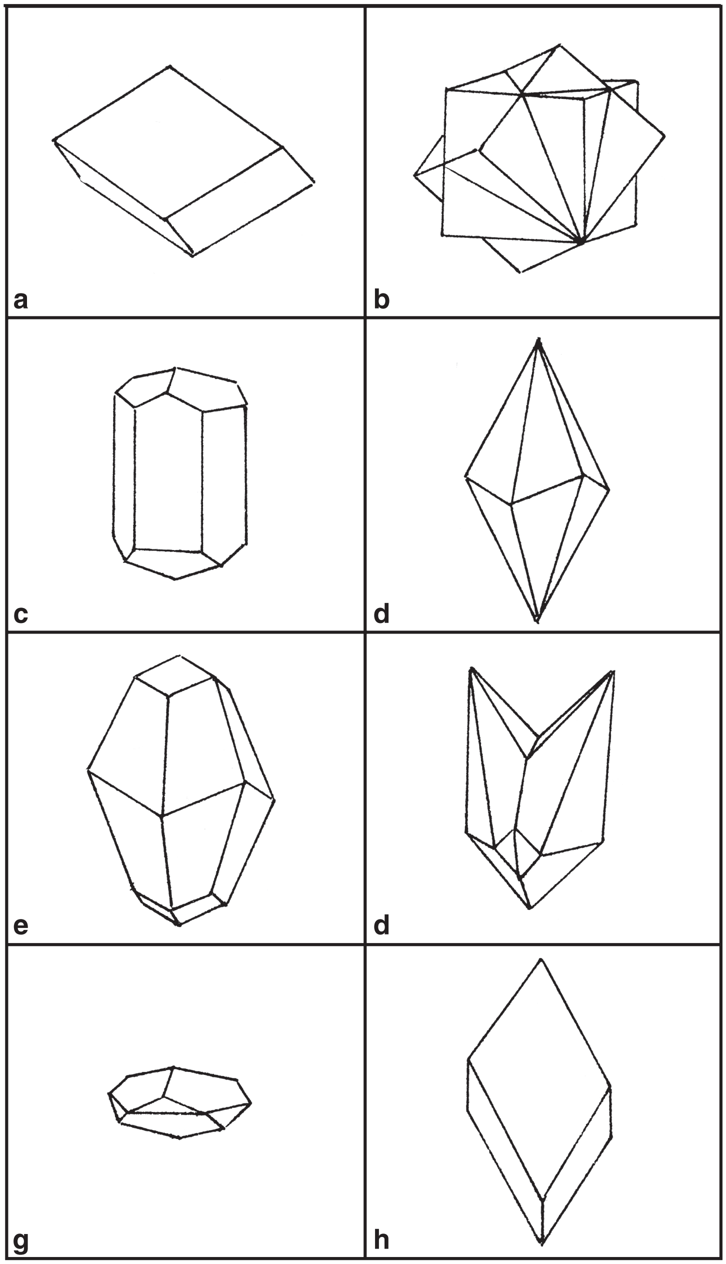

Figure 21 Calcite habits typical of Keokuk geodes: (a) Positive rhombohedron; (b) pseudocubic rhombohedron with a penetration twin; (c) hexagonal prismatic crystal rhombohedral terminations; (d) scalenohedron or dogtooth; (e) scalenohedron with rhombohedral terminations; (F) twinned scalenohedrons; (g) compressed negative rhombohedron; (h) crystal reflecting the true unit cell. *Source*: Sinotte, S.R., 1969, *The Fabulous Keokuk Geodes, Volume I*. Des Moines, Iowa: Wallace-Homestead Co. ©1969 Stephen R. Sinotte. Used by permission of the author.

Figure 22 Nailhead" or "scepter" calcite (7 cm) from Hamilton, Illinois. Similar calcites with the early scalenohedron capped with a later rhombohedron are found in geodes. Photograph by Kevin Conroy.

Figure 23 Similar generations of calcite growth habits are found in the Upper Mississippi Valley Lead–Zinc District approximately 199 mi (320 km) northeast of Hamilton, Illinois. Calcite (9 cm) from the Blackstone Mine in Shullsburg, Wisconsin. From the collection of Jared Freiburg. Photograph by Jeff Scovil.

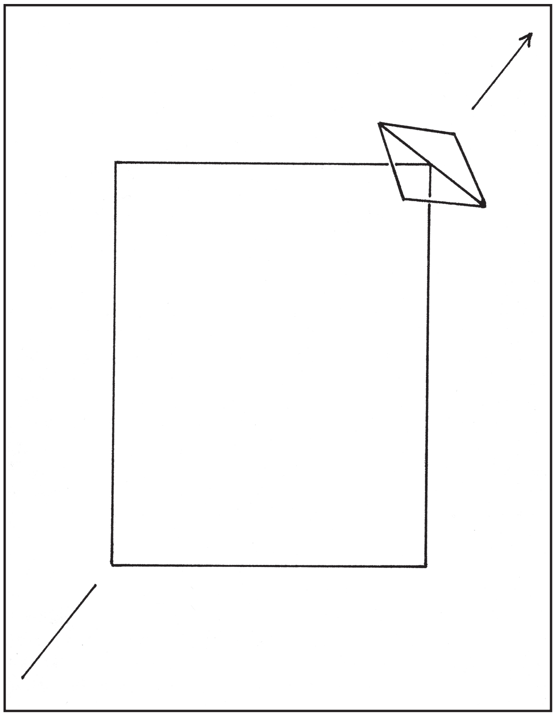

Figure 24 Epitaxial orientation of brown pseudocube and small clear rhombohedron calcite crystals in C-type and SC-type geodes. *Source:* Sinotte, S.R., 1969, *The Fabulous Keokuk Geodes, Volume I*. Des Moines, Iowa: Wallace-Homestead Co. ©1969 Stephen R. Sinotte. Used by permission of the author.

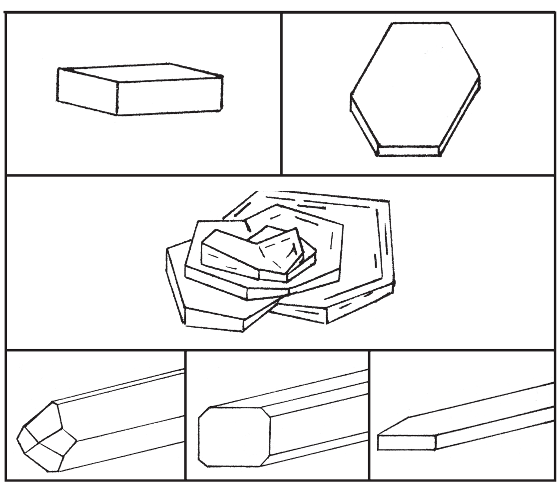

Figure 26 Three principal habits of barite crystallization found in Keokuk geodes: (top row) tabular orthorhombic crystals; (middle row) rosette groups of twinned, tabular, orthorhombic crystals; and (bottom row) long, slender orthorhombic prisms. *Source*: Sinotte, S.R., 1969, *The Fabulous Keokuk Geodes, Volume I*. Des Moines, Iowa: Wallace-Homestead Co. ©1969 Stephen R. Sinotte. Used by permission of the author.

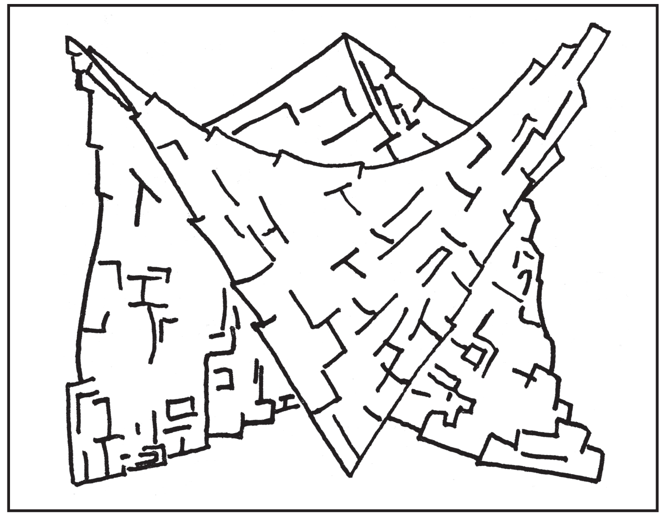

Figure 25 A saddle-shaped rhombohedron of dolomite found in geodes. *Source*: Sinotte, S.R., 1969, The Fabulous Keokuk Geodes, Volume I. Des Moines, Iowa: Wallace-Homestead Co. ©1969 Stephen R. Sinotte. Used by permission of the author.

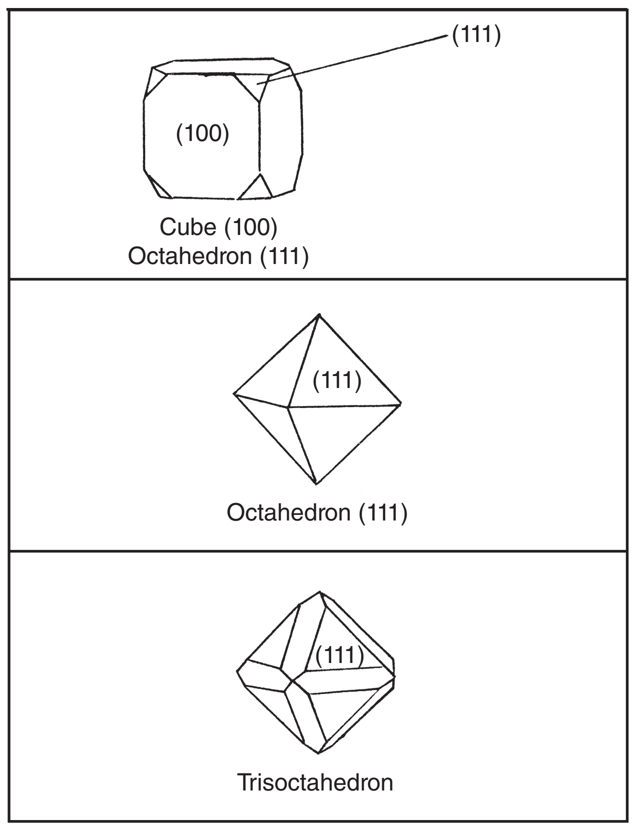

Figure 27 Pyrite crystal habits found in geodes showing the cube modified by the [111] octahedral faces, the true octahedron, and the trisoctahedron. *Source*: Sinotte, S.R., 1969, *The Fabulous Keokuk Geodes, Volume I*. Des Moines, Iowa: Wallace-Homestead Co. ©1969 Stephen R. Sinotte. Used by permission of the author.

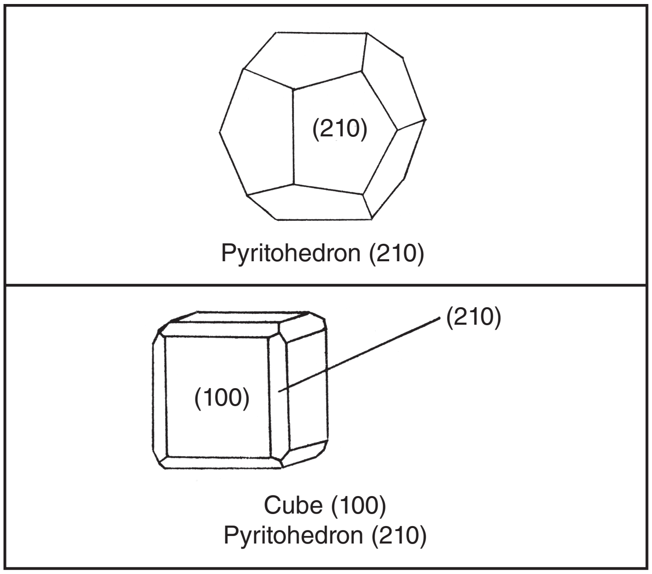

Figure 28 Pyrite crystal habits found in geodes showing the pyritohedron and the cube with edges beveled by the pyritohedral modifications. *Source*: Sinotte, S.R., 1969, *The Fabulous Keokuk Geodes, Volume I*. Des Moines, Iowa: Wallace-Homestead Co. ©1969 Stephen R. Sinotte. Used by permission of the author.

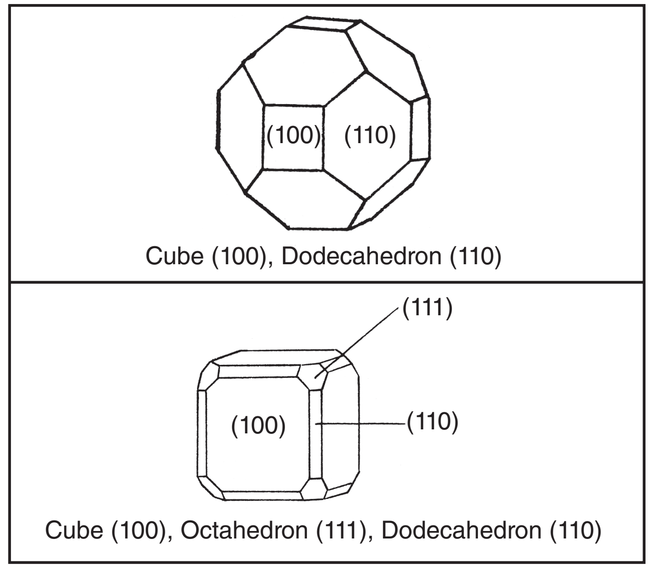

Figure 29 Pyrite crystal habits found in geodes showing the dodecahedron and the combined form of the cube, octahedron, and dodecahedron. *Source*: Sinotte, S.R., 1969, *The Fabulous Keokuk Geodes, Volume I*. Des Moines, Iowa: Wallace-Homestead Co. ©1969 Stephen R. Sinotte. Used by permission of the author.

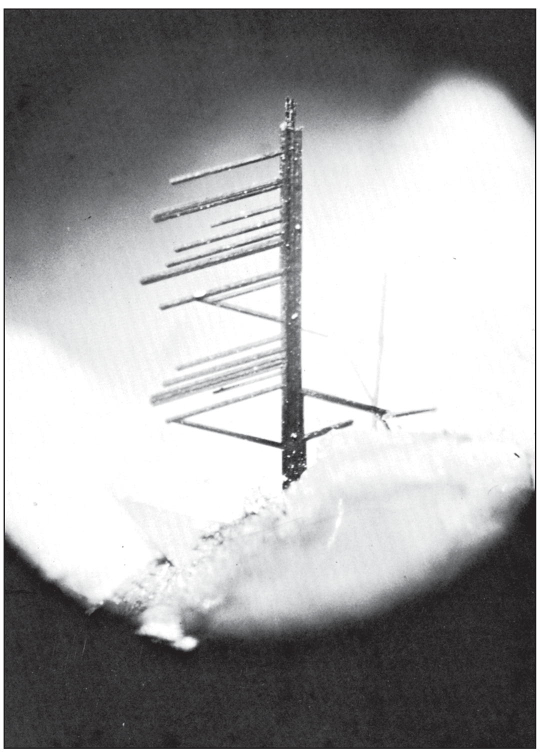

Figure 30 Reticulated crystals of marcasite in a geode. Crystals are rarely more than 2 cm in length and 1 mm wide. *Source*: Sinotte, S.R., 1969, *The Fabulous Keokuk Geodes, Volume I*. Des Moines, Iowa: Wallace-Homestead Co. ©1969 Stephen R. Sinotte. Used by permission of the author.

barite, and sphalerite. Calcite often exhibits phantoms formed by marcasite “dusting” between calcite growth generations.

Chalcopyrite

Chalcopyrite is rare in geodes. It typically forms sphenoids of dull to brilliant crystals measuring up to 2 mm (Figure 31). Chalcopyrite crystals are often oxidized to malachite, chalcocite, or tenorite.

Sphalerite

Sphalerite occurs as black, splendent, complex to distorted crystals measuring up to 8 cm across. Crystals form as dodecahedrons to octahedrons (Figure 32). Sphalerite is most commonly associated with blue barite, dolomite, kaolinite, quartz, calcite, and marcasite (Figure 33). It usually grows directly over the quartz crystals lining the geode and occasionally on botryoidal chalcedony. Fluid inclusion analysis of sphalerite in geodes suggests that the temperatures of deposition ranged from 70 to 95 °C and the chemistries resembled sphalerite in the Upper Mississippi Valley Lead-Zinc District (Field 2017).

Wurtzite

Wurtzite, an extremely rare polymorph of sphalerite, has been found in geodes. Wurtzite forms hexagonal pyramidal crystals. The photograph in Figure 34 represents the largest wurtzite crystal ever found in a geode. Until the discovery of the wurtzite at Merelani Hills, Tanzania, it was the largest known wurtzite crystal in the world.

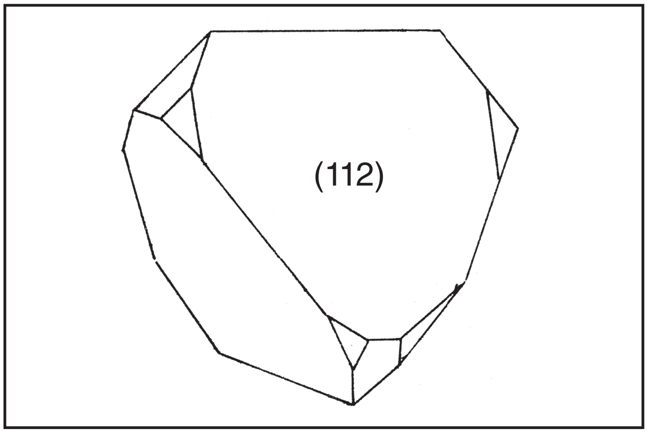

Figure 31 Tetrahedral crystal of chalcopyrite with disphenoidal faces (112) are often striated and may be found in geodes. *Source*: Sinotte, S.R., 1969, *The Fabulous Keokuk Geodes, Volume I*. Des Moines, Iowa: Wallace-Homestead Co. ©1969 Stephen R. Sinotte. Used by permission of the author.

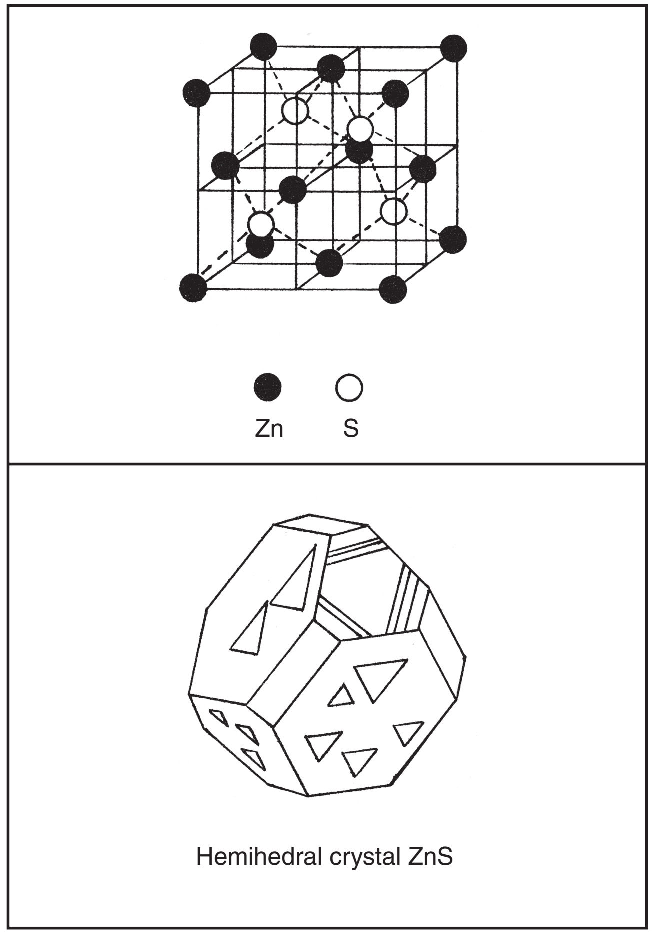

Figure 32 Sphalerite unit cell and crystal habit. *Source*: Sinotte, S.R., 1969, *The Fabulous Keokuk Geodes, Volume I*. Des Moines, Iowa: Wallace-Homestead Co. ©1969 Stephen R. Sinotte. Used by permission of the author.

Figure 33 Keokuk geode with sphalerite (2.5 cm), dolomite, quartz, and kaolinite over a chalcedony shell. Photograph by Kevin Conroy.

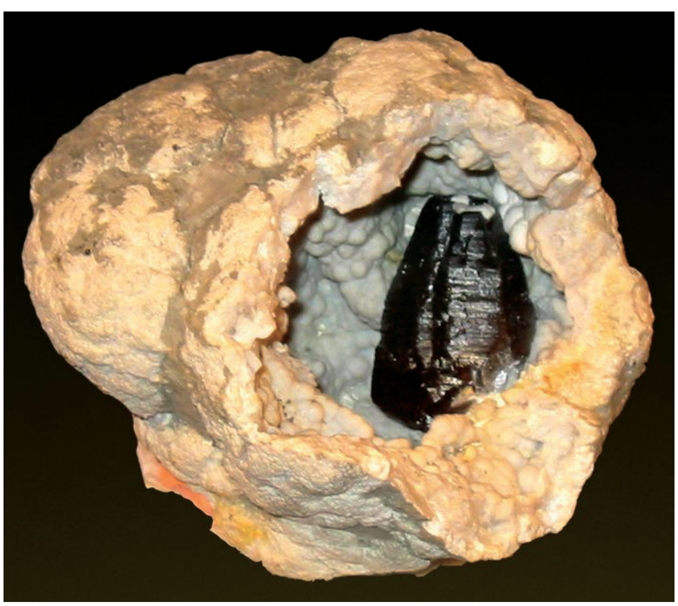

Figure 34 Wurtzite crystal (4.1 cm) in an S-type geode from the Hamilton Quarry. Found by Dr. R.G. Sinotte in 1953. Pfeiffer Foundation Museum specimen, Piggott, Arkansas. Photograph by John Rakovan. *Source*: Sinotte, S.R., 1969, *The Fabulous Keokuk Geodes, Volume I*. Des Moines, Iowa: Wallace-Homestead Co. ©1969 Stephen R. Sinotte. Used by permission of the author.

Goethite

Goethite most commonly forms as black, single-capillary crystals measuring up to 7 mm. In some occurrences, two or more crystals are found in subparallel positions and are always associated with quartz crystals. These crystals are generally associated with geodes containing sulfides. Goethite also occurs as earthy or loose coatings and iridescent or varnish-like stains on quartz and calcite, or as sharp pseudomorphs after iron pyrite, marcasite, and dolomite. Earthy tan to brown material has previously been misidentified as limonite and later shown to be hydrous goethite.

Hematite

Hematite is rare and can be observed as dark red tabular crystals measuring up to 1 mm, as a red earthy powder to a granular crust, as pseudomorphs after goethite, and as a red stain on quartz.. Hematite is often associated with early quartz and calcite.

Pyrolusite

Pyrolusite occurs as inclusions, subcrystalline aggregates on quartz, or black dendritic growths on calcite. It is also sometimes observed as black stains in chalcedony-lined geodes.

Malachite

Malachite occurs as a green alteration product of chalcopyrite. In rare cases, it appears as emerald-green subfibrous growth structures or macroscopic spots on quartz crystals.

Tenorite

Tenorite is very rare in Keokuk geodes. It occurs as a dark brown to black alteration product of chalcopyrite.

Selenite

Selenite commonly occurs as clear, elongated prisms measuring up to 4 cm. It forms as single crystals or as stellate or radial growths (Figures 35 and 36). Selenite is a common overgrowth on quartz, chalcedony, and, in rare cases, calcite.

Stilpnosiderite

Siderite does not occur in Keokuk geodes as individual crystals but rather is found as a thin, often iridescent film coating brown calcite crystals in C-type and SC-type geodes. This coating over calcite crystals results in beautiful iridescent calcite-lined geodes.

Jarosite

Jarosite is an ochre yellow to brown earthy powder often mistaken for limonite. It frequently coats pyrite and marcasite as a weathering alteration product. Pseudocubic and tabular jarosite crystals with a resinous luster have been observed in weathered geodes and may previously have been mistaken for sulfur.

Kaolinite

Kaolinite occurs as a snow white to brown earthy, highly crystalline powder within the geode cavity. It is believed to be the first mineral to form in the geode. Excessive amounts of kaolinite are found within the geode cavity as well as in discrete pockets within chalcedony euhedrons. Kaolinite is commonly associated with botryoidal chalcedony, dolomite, sphalerite, blue barite, and rhombic calcite. It is thought to have considerable influence on the outcome of subsequent mineralization because it is ingested during later mineral growth, resulting in structural and color alterations (Sinotte 1969). Calcite exhibits the most obvious alteration resulting from kaolinite ingestion. Sinotte (1969) suggested kaolinite might inhibit the growth of rhombohedral calcite or, when ingested, alter the crystal structure to cause scalenohedral growth. This argument is supported by X-ray diffraction (XRD) data showing strong patterns of both calcite and kaolinite in scalenohedral calcite and rhombohedral calcite devoid of kaolinite patterns (Hayes 1964). Sinotte (1969) also proposed that pink-colored scalenohedral calcites are the result of kaolinite ingestion. Other minerals that exhibit physical changes caused by the ingestion of kaolinite include barite, dolomite, and sphalerite. Barite is often colored a light blue when associated with kaolinite. Sphalerite has not been observed in the absence of kaolinite and often produces a light green color and a waxy luster with abundant kaolinite ingestion.

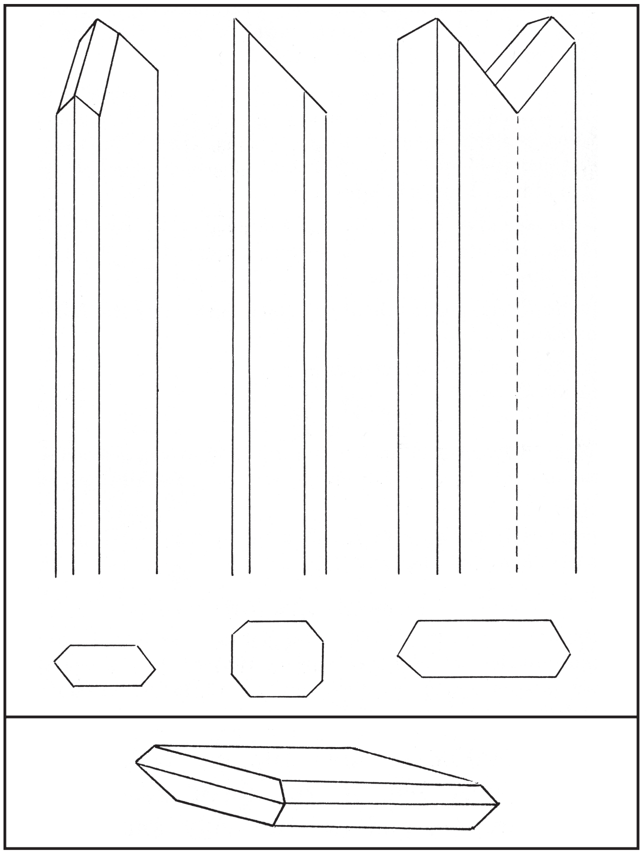

Figure 35 Three types of selenite terminations found in geodes. *Source*: Sinotte, S.R., 1969, T*he Fabulous Keokuk Geodes, Volume I*. Des Moines, Iowa: Wallace-Homestead Co. ©1969 Stephen R. Sinotte. Used by permission of the author.

Figure 36 Selenite in a quartz-lined geode (S-type) measuring 4 cm in diameter. Pfeiffer Foundation Museum specimen, Piggott, Arkansas. *Source*: Sinotte, S.R., 1969, *The Fabulous Keokuk Geodes, Volume I*. Des Moines, Iowa: Wallace-Homestead Co. ©1969 Stephen R. Sinotte. Used by permission of the author

KAOLINITE ORIGIN

The paragenetic relationship between kaolinite and other minerals in the geode indicates that kaolinite formed early. Kaolinite originated from fine-grained silicate residue remaining after the dissolution of early calcareous concretions (Van Tuyl 1912). Hayes (1963) expanded this hypothesis into a theory that accounts for the following observations:

1. Kaolinite is present only in the upper mudstone unit of the lower Warsaw.
2. The concretions from which kaolinite-bearing geodes developed contained substantial amounts of silicate minerals, including clay minerals, but no kaolinite (Figure 37).
3. Kaolinite is absent from geodes containing remnants of the original concretion calcite (Figure 37).
4. No other clay minerals, such as those found in concretions, occur with kaolinite geodes.
5. The ingestion of kaolinite by calcite euhedrons and other minerals indicates that kaolinite genesis predates the growth of all other minerals in geode cavities and was very early in geode paragenesis.

Hayes (1963) concluded that the acid that formed the concretion cavity also reacted with silicate residue left behind by the dissolution of the concretion clay minerals. Any leftover concretion calcite suggests the entering pore fluid was neutralized and thus unable to react with the silicates. The conversion of silicates such as illite, chlorite, and perhaps quartz to kaolinite likely occurred at about pH 4, where alumina is highly mobile.

The geochemistry of kaolinite deposition is obscure. A typical kaolinite-filled Keokuk geode may contain up to 15 g of kaolinite. The volume of solution required to bring in the alumina would be more than 528,344 gallons (2 million liters), based on conventional solubility data (Keller 1970). Keller (1978) suggested that complexed ions of aluminum with organic matter, which resulted in more concentrated aluminum solutions, might have provided aluminum transport. Another possibility is that solutions of hydrophilic colloids of polymeric aluminum hydroxide supplied the aluminum for the formation of kaolinite in geodes (Yariv and Cross 2012).

KAOLINITE MINERALOGY

Keokuk kaolinite is very crystalline kaolinite compared with other types, such as Georgia kaolins. Furthermore, it can be collected and purified quite easily without grain size separation. For these reasons, the structure of kaolinite has been refined by using Keokuk kaolinite (e.g., see Bish and Von Dreele 1989). Quartz and calcite are often found when analyzing scraped clay. Sieving to 63 mm will often remove both quartz and calcite, after which the only mineral that can still be detected in minor amounts is dickite, a polymorph or polytype of kaolinite. Dickite typically forms at higher temperatures (>120 °C), which suggests that the geodes have been exposed to temperatures greater than 120 °C.

The samples used for XRD and SEM analyses were collected by scraping the clay out of the geode (see front cover), making a grain mount on carbon tape, and then carbon coating the powder for SEM and side packing the powder for XRD by cobalt radiation. Further studies of Keokuk kaolinite not discussed here include (1) thermal analysis (e.g., Keller et al. 1966, which reports an elevated dihydroxylation temperature), (2) infrared studies (e.g., Prost et al. 1989; Johnston et al. 1990), and (3) Raman spectroscopy (e.g., Shoval et al. 2002).

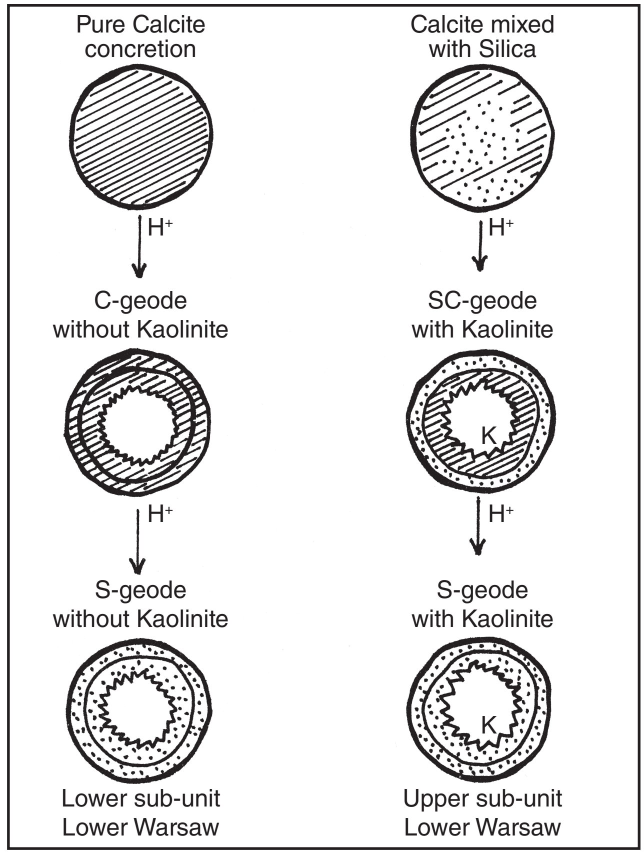

Figure 37 Schematic representation of the formation of C-type, SC-type, and S-type geodes from calcite concretions. *Source*: Sinotte, S.R., 1969, *The Fabulous Keokuk Geodes, Volume I*. Des Moines, Iowa: Wallace-Homestead Co. ©1969 Stephen R. Sinotte. Used by permission of the author.

X-ray Diffraction

Bish and Von Dreele (1989) used Keokuk kaolinite to refine the structure of kaolinite. Figure 38 shows a close-up of their XRD and Rietveld modeling results, and Figure 39 shows a comparison of their results with ours. We detected some quartz, which could easily be removed with further sieving. Bish and Von Dreele (1989) noted an absence of two-dimensional diffraction effects in Keokuk kaolinite. This can be observed when comparing the intensities of the 00l reflections with hkl reflections, making it ideal for structural refinements. However, dickite peaks that did not overlap the kaolinite peaks were also detected (Figure 39).

Scanning Electron Microscopy

The crystallinity of Keokuk kaolinite can also be seen under SEM (Figure 40). Crystal faces can be seen in all three dimensions along the cleavage, not just two-dimentional planes that are typical of sheet silicates. The size of an individual crystal is at least 5 × 5 × 5 µm. Kaolinite typically has the largest dimension in the direction perpendicular to the cleavage direction, although this can be observed only occasionally in our analyses. The morphology could be easily be mistaken for dickite, which typically has blocky crystallites.

CONCLUSION

This concludes the informational guide for our trip to hunt for kaolinite in the famous geodes within the Hamilton–Keokuk area. We hope the trip has been a great success and you have obtained samples of the highly ordered kaolinite and geodes exhibiting other beautiful associated minerals outlined in this guide. These kaolinite-filled geodes are a unique phenomenon controlled by local and regional geology that offer insight into the complex diagenetic history of the rock. Questions about geode and kaolinite origins remain. We hope this trip has inspired discussion on kaolinite that ultimately will lead to more research on its genesis.

ACKNOWLEDGMENTS

We acknowledge Dr. Stephen Sinotte for his generosity in providing figures from *The Fabulous Keokuk Geodes, Volume I* (1969), which is often regarded by geode collectors as the seminal book on Keokuk geodes. We also thank Susan Krusemark, Michael Knapp, Christopher Korose, and Daniel Byers of the Illinois State Geological Survey for their excellent work editing, designing, and providing figures for this guidebook. Last, we thank the Illinois State Geological Survey for donating time and resources, which greatly contributed to the completion of this guidebook.

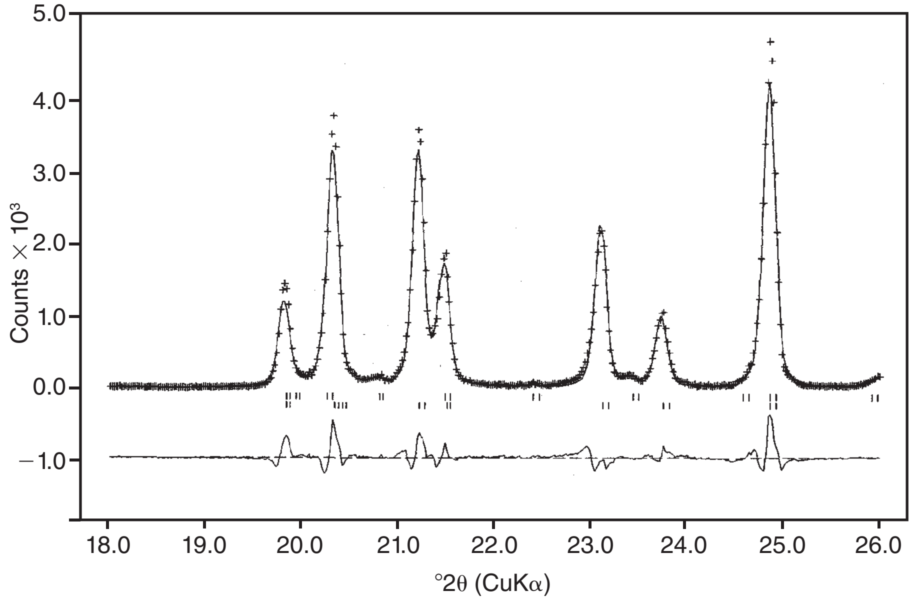

Figure 38 Experimental and modeled X-ray diffraction traces of the Keokuk kaolinite. Figure 2 from: Bish, D.L., and R.B. Von Dreele, 1989, Rietveld refinement of non-hydrogen atomic positions in kaolinite: Clays and Clay Minerals, v. 37, no. 4, 289–296. Reproduced with kind permission of The Clay Minerals Society, publisher of *Clays and Clay Minerals*.

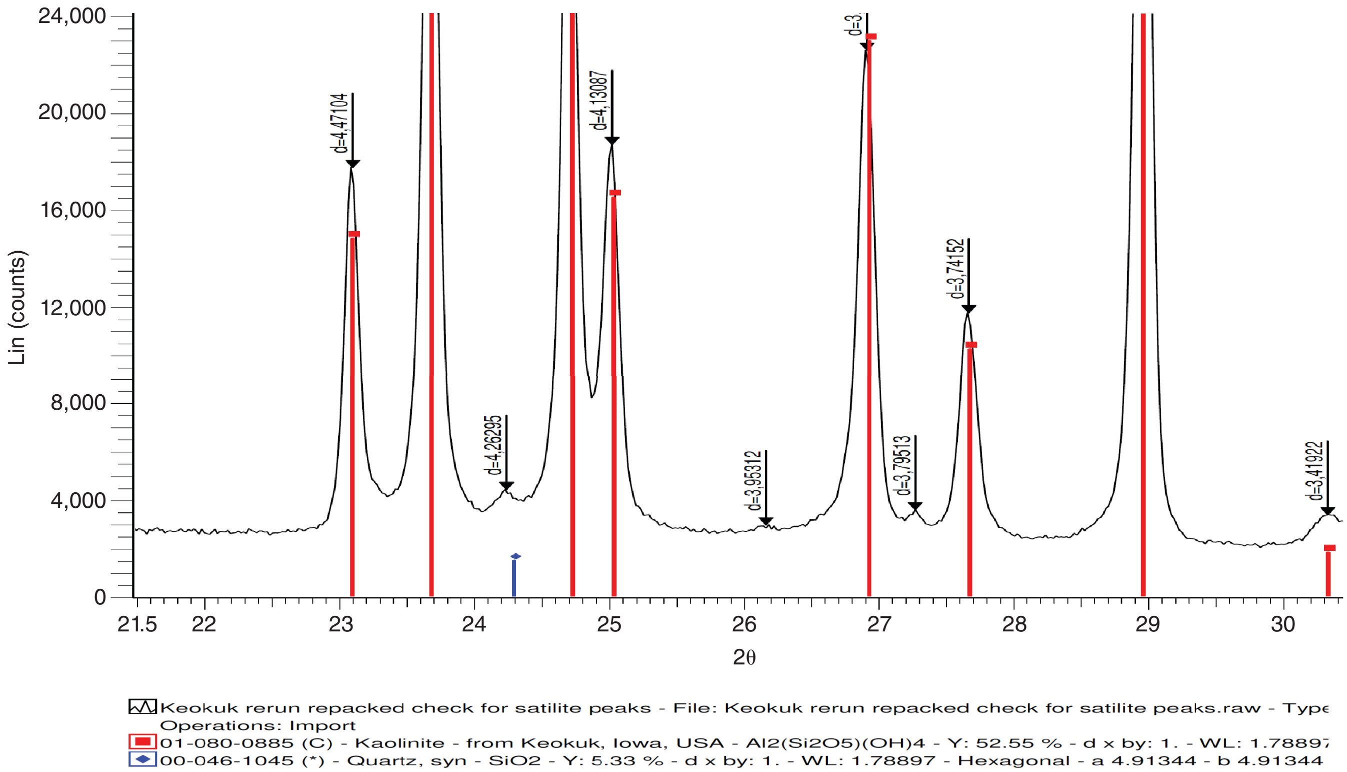

Figure 39 Detailed X-ray diffraction pattern of Keokuk kaolinite powder showing the similarity in peak intensities to those of Bish and Von Dreele (1989; see Figure 38). Peaks in red are kaolinite, the peak in blue is quartz, and peaks that are exclusively dickite are labeled with their d-spacing. Cobalt radiation was used. For the full X-ray diffraction pattern, see the Appendix.

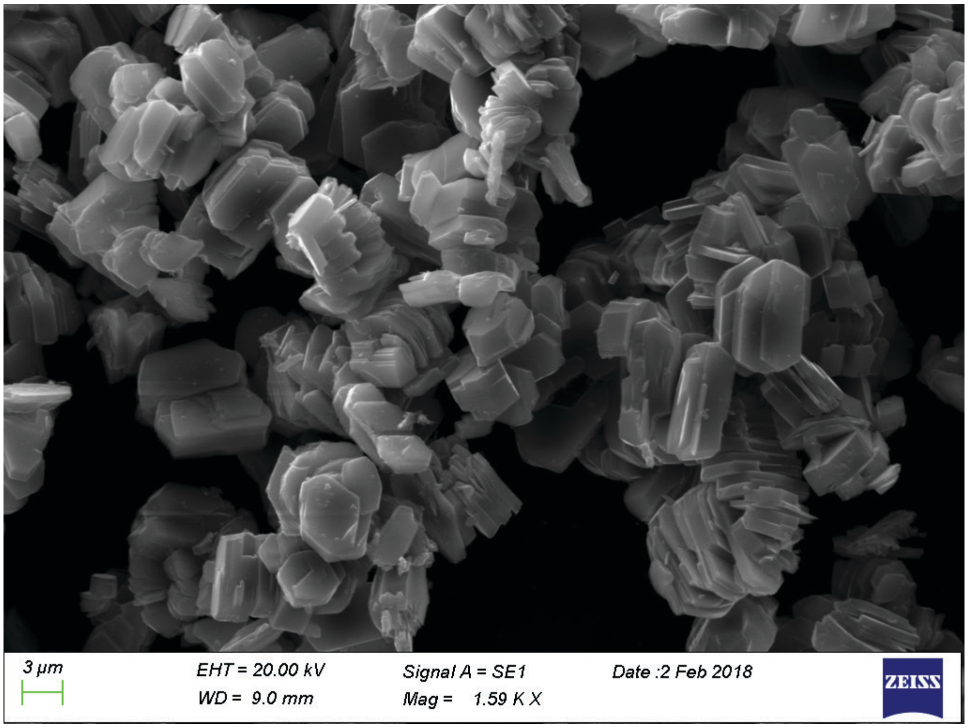

Figure 40 Keokuk kaolinite scanning electron photomicrograph of a powder mount.

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APPENDIX

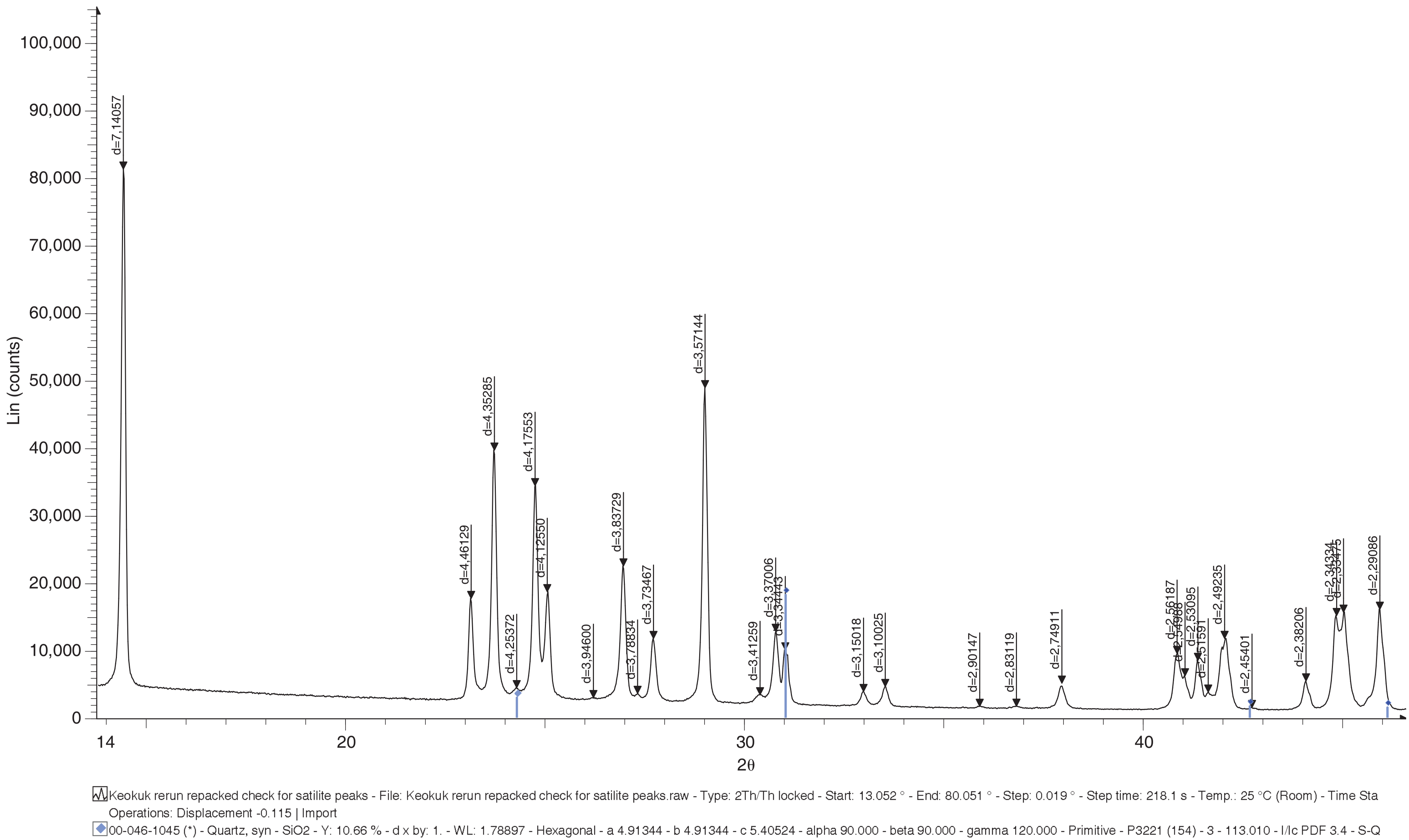

Figure A1 X-ray diffraction pattern of Keokuk kaolinite, Part 1. Bruker D8, cobalt radiation, LynxEye detector.

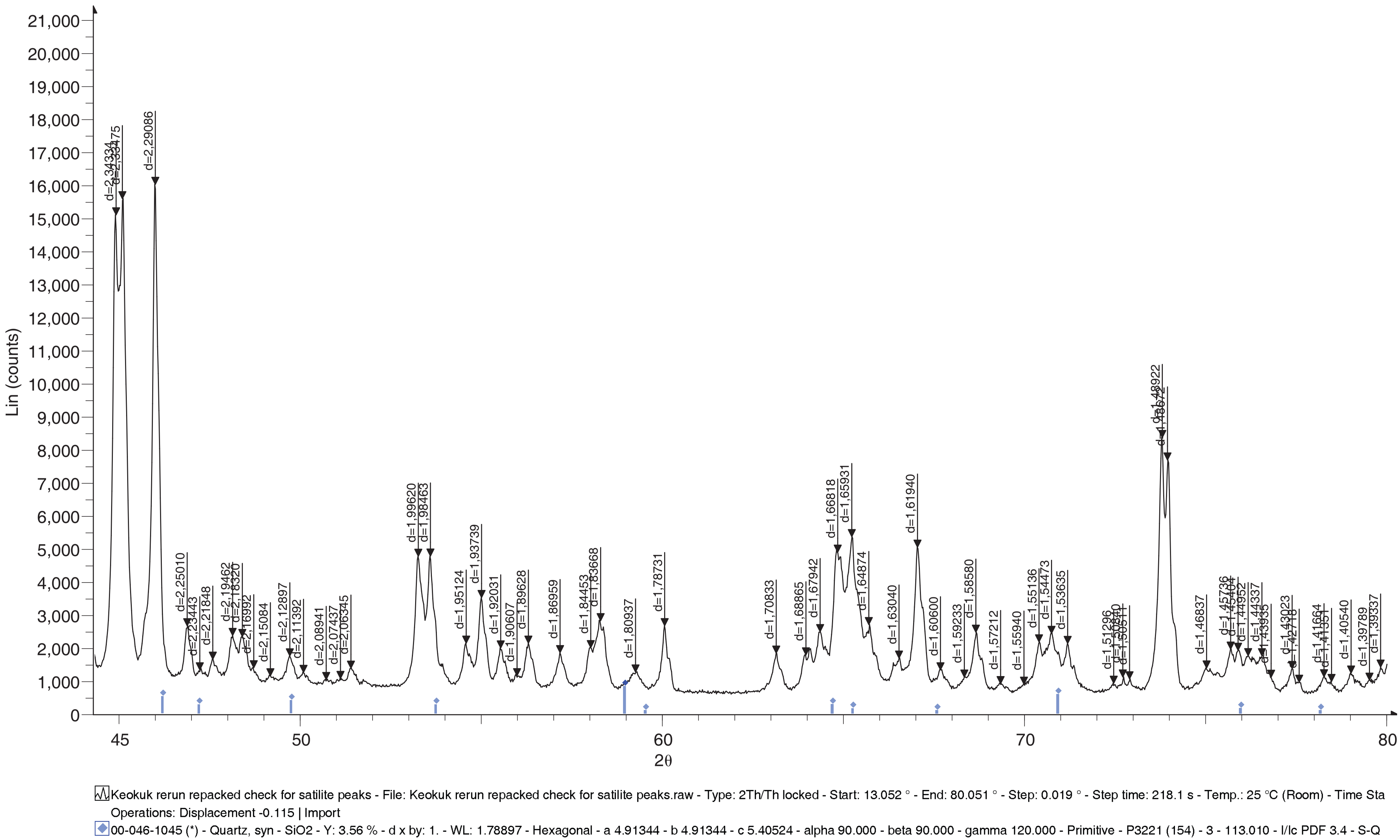

Figure A2 X-ray diffraction pattern of Keokuk kaolinite, Part 2. Bruker D8, cobalt radiation, LynxEye detector.