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A Review of the Deposition and Alteration of Filled-Sink Deposits of East-Central Missouri

by

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A REVIEW OF THE DEPOSITION AND ALTERATION OF FILLED-SINK DEPOSITS OF EAST-CENTRAL MISSOURI

Sigrid Asher-Bolinder

Abstract

The filled-sink deposits of Atokan age of east-central Missouri occur on the remnants of a Pennsylvanian erosion surface dipping north from the Ozark dome. They consist of cup-shaped rims of steeply dipping sandstone containing centripetally dipping infilling rocks of varying composition. The inward-dipping Cheltenham rocks and their massive-to-fractured Graydon sandstone rim rocks lie within relatively undistorted, primarily Ordovician, country rock, suggesting that filled sinks continued to subside apace with their filling. Modern analogues of such features and mineralogies have not been noted, although their general shape resembles that of sinkholes.

Some filled sinks in the southern portion of the filled-sink region contain marcasite and(or) pyrite passing upward to hematite; sinks in the central region contain iron-rich flint clay and flint clay of varying economic grades, burley clay, and böhmite and(or) diaspore; and to the northern part of the region are kaolinitic and illitic clays. Some filled sinks contain coal beds. Surface and groundwater leaching and desilication of the fluvial, paludal, and marine(?) sediments that fill the sinks have been invoked to explain their present composition, although such a process seems unlikely to have formed marcasite and(or) pyrite deposits.

Post-Atokan erosion has removed the upper layers of filled-sink deposits and the surrounding rocks, leaving an unclear picture of the terrain that led to their deposition on the flanks of the Ozark uplift. However, their proximity to Mississippi Valley-type deposits, the distribution of iron sulfides, and the rare presences of uranium, copper, and lithium minerals in the Cheltenham rocks suggest mechanisms other than leaching and desilication to explain their present-day composition and distribution. Alteration of filled-sink sediments by fluids related to Mississippi Valley-type deposits and(or) hydrothermal fluids which interacted with the underlying Precambrian volcanic rocks may have determined their present mineralogies.

INTRODUCTION AND ACKNOWLEDGMENTS

The filled-sink deposits of east-central Missouri have been a source of plastic and flint clays, refractory materials such as diaspore and böhmite, coal, and iron and sulfur ores from 1815 A.D., or before, to present (Crane, 1912; Rueff, 1988). However, the origins of the filled sinks and the paragenesis of their deposits is still debated (Keller and Stevens, 1983; Tourtelot and others, 1990). This review of the existing literature was undertaken to better understand the factors that controlled the occurrences of anomalous quantities of lithium in some flint clays (Tourtelot and Brenner-Tourtelot, 1978).

Many different terms, some of which reflect usage by ceramic and refractory industries in Missouri, appear in the literature to describe the contents of filled sinks. Commercial products discussed in this report are described by their authors as fire clays, flint clays, burley clays, plastic clays, bauxite, and refractories. Fire clays are siliceous and high in hydrous aluminum silicates--mostly kaolinite (better grades contain at least 35 percent alumina when fired)--and are deficient in iron, calcium, and alkalies. They have high temperatures of fusion and are suitable refractory or ceramic materials. Flint clays are very hard, smooth fire clays that break with a conchoidal fracture, do not dissolve when wetted, exhibit no plasticity when ground, and are composed primarily of halloysite (Gary and others, 1977) or well-ordered kaolinite (Keller and Stevens, 1983). Flint clays may also contain diaspore and böhmite. Burley clays are mixtures of kaolinite, böhmite, and diaspore (Keller and Stevens, 1983) and are so-called because of the ooids, or burls, of diaspore that occur in the kaolinite matrix. Plastic clays are those which have lower temperatures of fusion and deform plastically when ground; they consist of mixtures of less well-ordered kaolinite and illite. Bauxites are "a mixture of various ... hydrous aluminum oxides and aluminous hydroxides, principally gibbsite, some boehmite, and containing impurities in the form of free silica, silty, iron hydroxides, and esp. clay minerals" (Gary and others, 1977). In contrast, böhmite and diaspore are not clays, but are dimorphic forms of $AlO\cdot(OH)$, and they are major constituents of some bauxites. Refractories, or refractory clays, are fire clays.

Hematite is common constituent of flint clays, and it may also be the main fill of sinks in the southern part of the flint-clay region. In an iron oxide-stained flint clay of the Schaefferkoetter deposit, the iron-containing mineral may be diadochite (Keller and Stevens, 1983). However, the hematite that fills the sinks in the southern region is the product of oxidation of marcasite and pyrite, and it seems to be unrelated to the presence of clays. Both soft red hematite and blue specular hematite are present, as are lesser amounts of limonite.

Several people have contributed to my interest in the origins and minerals of filled sinks. Allen Heyl, formerly of the U.S. Geological Survey, reminded me of their proximity to Mississippi Valley type Pb-Zn-Cu deposits. H.A. Tourtelot, U.S. Geological Survey, shared his extensive knowledge of filled sinks and their minerals, served as sounding board to various ideas, and graciously reviewed this paper. Ira Satterfield and Ardel Rueff of the Missouri Department of Natural Resources arranged memorable field observations to compare with the literature on filled sinks of the last eighty years. I thank them all.

DESCRIPTION OF FILLED SINKS

Geographic and stratigraphic distribution of filled sinks and their related lithologies

The filled sinks of central Missouri are located primarily south of the Missouri River in Cole, Moniteau, Morgan, Franklin, Gasconade, Osage, Miller, Maries, Phelps, Dent, and Crawford Counties, with lesser occurrences in Pettis, Cooper, Dallas, Texas, Reynolds, Iron, and Washington Counties. Gasconade, Crawford, and Osage Counties contain the largest numbers of fire-clay and refractory-minerals deposits; the majority of hematite deposits, with or without pyrite, occur to the southeast in Crawford, Phelps, and Dent Counties. To the northwest of the fire-clay and refractory-materials zone, in Moniteau, Morgan, and Miller Counties, the concentration of coal-filled and coal-and-fire-clay-filled sinks is highest. Figure 1 shows the distribution of filled sinks and their contents in the late 1940's; knowledge of the localities and contents of the filled sinks is rapidly lost to public record after their mining due to the quick overgrowth of vegetation, their filling with water, and deep weathering in a humid climate.

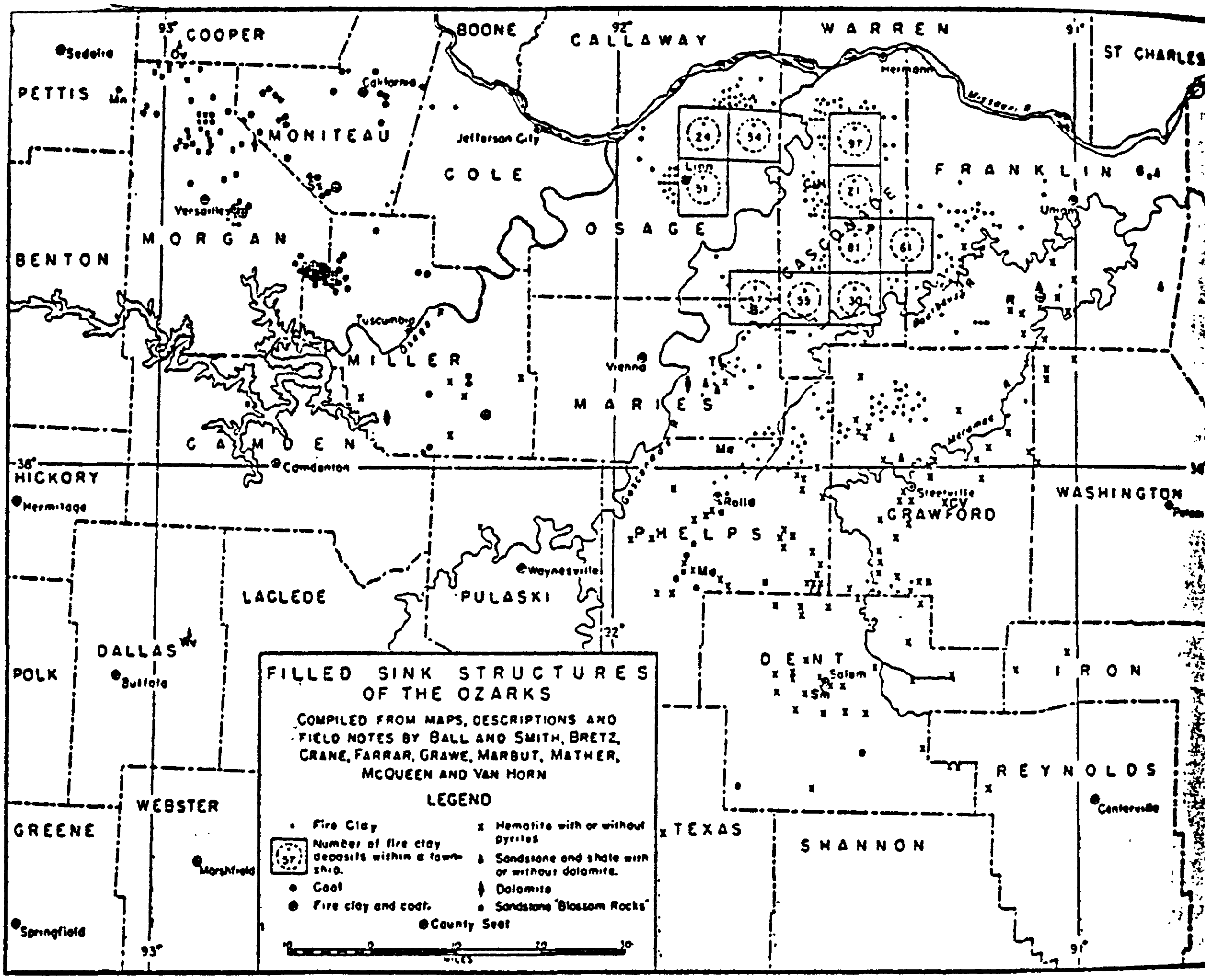

Figure 1.--Localities of filled sinks (modified from Bretz, 1950), east-central Missouri.

Today's topography is, to some degree, a further denuded and more incised version of the topography on which the filled sinks developed. However, the region was subject to mild folding and faulting both before and after deposition of the filled sinks' contents (McQueen, 1943). Thus, distribution of known filled sinks shows some degree of structural, as well as late-Pennsylvanian erosional-surface, control. In the central and southern filled-sink region--sites of flint clays, associated refractory materials, and iron ores--older Cambrian formations are exposed higher on the flanks of the Ozark dome, whereas, nearer the Missouri River, lower on the flanks of the dome, near the Missouri River, surface exposures are remnants of Ordovician St. Peter Sandstone (Anderson and others, 1979). Devonian and Kinderhookian- through Meramecian-stage Mississippian marine rocks are sparsely preserved in the filled-sink region, indicating that these marine units were deposited before the development of an extensive erosion surface in Chesterian through early Pennsylvanian (pre-Atokan?) time on the north and northwest flanks of the Ozark dome (Anderson and others, 1979).

The pre-Atokan low-relief fluvial and paludal surface was first a site of chemical and physical erosion, and, later, deposition of low-energy fluvial, paludal, and marine(?) sediments. Residuum of chert boulders, sands, and clays originally blanketed the region. Although much of this Pennsylvanian-age cover has been subsequently removed, its remnants are known as the Graydon sandstone (Missouri usage). The Graydon varies widely in lithology from one part of the filled-sink region to another. It contains clay and coal in some regions and chert conglomerate and(or) breccia in others. It is pyritic and thus, sparsely gypsiferous, in some areas, and it is locally recemented to "quartzite" (McQueen, 1943, p. 36) in others. As the Graydon sandstone forms the basal fill and (possibly) the rim rock of the filled sinks of the region, as well as remaining as isolated upland remnants, understanding its provenance(s), environment(s) of deposition, and diagenetic history would better delineate the history of the surface upon which the filled sinks developed. Parikh (1970) presented petrographic evidence that the source for the rim rock sandstone northeast of Rolla, Missouri is most likely the St. Peter Sandstone, reworked, perhaps, from exposures higher on the Ozark dome.

Morphology of filled sinks and their relationship to enclosing rocks

Filled sinks exposed in road cuts and those recently mined for their flint clay or related minerals provide rare glimpses into the gross morphology of these unusual structures. The deposits are unconformable within the Ordovician through Mississippian marine country rocks that dip away from the Ozark dome. Keller and others, 1954, (p. 10)) state that the following formations are those "with which the clay-producing Pennsylvanian fill is most commonly seen in contact":

- Mississippian System
  - Burlington-Keokuk limestone
- Devonian System
  - (?)Callaway limestone
- Ordovician System
  - (?)Kimmswick limestone
  - Jefferson City dolomite
  - Roubidoux sandstone and dolomite
- Cambrian System
  - Gasconade dolomite

Note that the age of the Gasconade is now held to be Ordovician. The Jefferson City Formation is indistinguishable in the field from the Cotter Formation in the filled sink region, and the two formations are often lumped together as "Jefferson City-Cotter" (A.R. Rueff, oral commun., 1990)

Filled-sink sediments lie within upward-expanding cone-shaped structures as deep as 150 ft (46 m); "The average deposit would probably measure 100 x 75 x 60 feet." (31 x 23 x 18 m) (McQueen, 1943, p. 140). Filled sinks are generally lined by several tens of centimeters to several meters of quartz-rich sandstone of varying induration, brecciation, and recementation; rarely are these sink walls--or rim rocks--limestone or chert. These rim rocks are unconformable with the surrounding country rock and dip steeply, sometimes nearly vertically to slightly overturned, inward.

Beds of cherty dolomite, sandstone, and shale that surround the filled sinks and rim rocks stop abruptly at the rim rocks, or they may dip gently inward toward the rim rocks, suggesting that downward movement of the fill and rim rocks continued during and after their deposition, forcing localized, generally downward, movement of the surrounding rock (Bretz, 1950).

The relationship between the narrow bases of the filled sinks with underlying country rock is less clear. Tourtelot and others (1990) report that drilling through the bottom of a filled sink recovered 120 feet (37 m) of "variably iron-stained, silica-cemented, and leached ... much disturbed" sandstone underlain by silica-cemented breccia of limestone and chert.

Filled sinks that have been mined have been at or near the surface. However, in some areas overlying the Graydon and Cheltenham Formations are thin Pennsylvanian marine units marking the resumed rise and fall of sea level and development of an erosion surface in later Pennsylvanian time (Keller, 1978, p. 242).

Orientation of sediments within the filled sinks

Original bedding in the clays, in the intervening zones of sandy clay, and in the sometimes intact rim rocks is often visible. Bedding now dips, in general, centripetally toward the center of the pit (McQueen, 1943), with the rim rocks nearly vertical to slightly overturned in places. Pyritic, hematitic, or cherty zones may occur between the rim rock and the country rock, clearly delineating the orientation of the beds. Coal beds within the filled sinks vary from near-horizontal to vertically slumped (H.A. Tourtelot, oral commun., 1990).

Minerals of the filled sinks

The filled sinks themselves contain a variety of rocks and minerals (Introduction and acknowledgments). The northwestern-most deposits contain coal as well as plastic clays (Bretz, 1950, p. 796). The progression generally southward from plastic to flint clays is accompanied by an increase in ordering of kaolinite, a decrease in illite, and a decrease in quartz. As a flint clay undergoes further ordering of its crystal structure, it also develops larger, well-ordered kaolin crystals. Keller (1978, p. 242) suggested that the illitic and kaolinitic residuum developed in Pennsylvanian swamps was leached of potassium, further kaolinitized, and desilicated shortly after deposition, via "upward and lateral leaching". The mechanism of upward movement of water was not specified.

Within a single clay-and-refractory-filled sink, a somewhat orderly zonation of the grades of clays and refractory materials may be evident. An excellent description of such zonation is provided by Keller and Stevens (1983) from the Schaefferkoetter diaspore and flint clay deposit northwest of Owensville, Gasconade County. From the rim rock to the central core, sandy clay passes into flint clay, to burley, to diaspore or böhmite. The clays vary inward from the pit margin also, from mixtures of quartz grains and illite-kaolinite "packets" to well-ordered kaolin. Alumina content of the deposit increases inward from 35 percent in the flint clay to 75 percent or greater in the "select" first-grade diaspore.

Keller (1979) suggested that filled sinks show a fairly orderly geographic progression from north to south of plastic clays, through semi-plastic and semi-flint clays, through flint clays, and generally more to the south, burley (a mixture of flint clay and ooids--"burls"--of diaspore), and diaspore and böhmite. McQueen and Gott's 1942 map (in McQueen, 1943, modified as plate 1, this report) does not support that concept; pits mined for their flint clays were present from the north to the south ends of the region, as were pits mined for their diaspore-burley content. Although flint pits and diaspore-burley pits were present from north to south, there was a tendency for like types of pits to cluster together.

In some flint clay (and burley clay, böhmite or diaspore) deposits are zones of "alkali-infested" clays not suitable for brick or refractory use. The "alkali" in some of those zones is as much as 5,100 ppm Li (whole-rock analysis) contained in a "dioctahedral chlorite nearly identical to the lithium-bearing chlorite "cookeite" ($LiAl_4(SiAl)_4O_{10}(OH)_8$)" (Tourtelot and Brenner-Tourtelot, 1978, see plate 1 this report).

Keller (1983) listed typical Li_2O values (converted here to parts per million Li) for flint clay, burley clay, and diaspore in the Schaefferkoetter pit:

Material	**Li_2O in percent (Li in ppm)**
Flint clay	0.10 (465)
Burley clay	0.37 (1,720)
Second-grade diaspore	0.29 (1,349)
Diaspore	0.15 (698)

Burley clay is believed to be derived from the further desilication of kaolinite, and it may be more porous than either flint clay or diaspore. Second-grade diaspore is gradational between burley clay and diaspore. Some diaspore deposits show accumulation of second-generation pore-filling diaspore within a coarser-grained diaspore structure (Allen, 1954). Thus, the distribution of lithium in the Schaefferkoetter samples may be associated with the degree of original porosity, and hence, room for later growth of a secondary lithium-containing minerals from solutions of unspecified composition and temperature.

Secondary mineralization of torbernite ($Cu(UO_2)_2(PO_4)_2 \cdot 8\text{-}12H_2O$) (Keller, 1952) and metatorbernite ($Cu(UO_2)_2(PO_4)_2 \cdot 8H_2O$) has been reported in flint clays of the region. The metatorbernite "was observed to occur chiefly on spheroidal masses of bad clay, so-called "sore spots" ... and was associated with barite, a small amount of chalcopyrite, and limonite" (Grawe *in* McQueen, 1943). At the Gieck Pit, north of Belle, fine-grained pyrite or marcasite surrounded diaspore oolites (Allen, 1935). Leaves of native copper "localized about black carbonaceous lumps in an oolitic diaspore flint clay" occur in a clay with "high content of alkalies and titania" (Allen, 1935, p. 19) suggest that "ground water solutions penetrated the clay after its deposition" (Allen, 1955, p. 398), although the source of the copper and alkalis in that ground water is unspecified.

Higher still on the Ozark dome, generally to the south of the flint clay-, diaspore-, and böhmite-filled sinks, occur sinks (now largely mined out and under water) filled originally with massive pyrite and marcasite. Much of the original pyrite and marcasite was replaced by hematite and limonite through oxidation at an unknown time in the past. Also in some iron-ore-bearing filled sinks "sulphide and carbonate of copper" were reported "occur[ing] most frequently in deposits containing unaltered marcasite" (Crane, 1912, p. 93-94). Filled-sink deposits of intimately mixed hematite and kaolinite occur in the zone transitional between the iron-bearing filled sinks and the kaolinite-bearing filled sinks. These red flint, or mixed, clays are used today in brick manufacture. However, flint clays with varying degrees and distributions of hematite occur throughout the filled-sink region.

THE ORIGINS OF FILLED SINKS AND THEIR DEPOSITS

Authors have suggested diverse mechanisms by which filled sinks could evolve. Although Bretz's (1950) hypothesis for the formation of filled sinks, "gradual subsidence of overlying rocks keeping pace with solutional removal, *under saturated conditions* (italics mine), of subjacent calcareous rock" (p. 790), offers an explanation of the formation of filled sinks, it does not address either the mechanism by which solutional removal of subjacent calcareous rock occurred or a pathway through which the solutions were carried away. While stating that "filled sinks of Missouri are very unusual results of ground-water work" (p. 831), and "deformation and subsidence of fill material is held to have closely accompanied the solutional removal of the underlying calcareous rock, no open cavities ever existing beneath the fills of these structures. *The pressure necessary to produce the structures was provided by once-overlying formations, long since stripped off in the peneplanation of the Ozark so-called dome.*" (p. 830, italics mine). Keller and others (1954) ascribed filled-sink origins to karstification; in 1983 Keller and Stevens stated that "Missouri high-alumina clay deposits, as components of a flint-clay facies, originated in a paludal, karstic environment, and that desilication took place as a phase of early diagenesis in the sediment before they were covered by younger Pennsylvanian-age rocks" (p. 432-433).

Whether the sedimentary processes that led to the infilling of the sinks were low-gradient fluvial and paludal, marine, or combinations thereof is unclear. However, present-day limestone solution sinkholes in western subtropical Florida develop when dissolution of the limestone *at the surface* occurs along highly transmissive joints in the vadose zone; downward solution, rather than upward stoping, is at work. When the sinkhole intersects the water table, leading to a decline in its rate of subsidence, sand and clay accumulate in the resulting funnel-shaped depression (Sinclair and others, 1985). In the case of the filled sinks of southeast Missouri, Pennsylvanian seas would have allowed sinks to develop over long periods of time--and over a wide area--as sea level continued to drop. As the water table fell and dissolution proceeded downward, sediments within the sinks sagged deeper into their centers, making room for more sediments to accumulate at the surface. Figure 2 suggests how a sandstone rim rock and centripetally dipping claystones and coals may have developed within a filled sink.

Because we do not have a clear picture of the Pennsylvanian surface upon which the filled sinks developed, we cannot easily explain possible stratigraphic or genetic relationships between iron- and clay-filled sinks. Pre- and post-depositional minor faulting and folding of the beds enclosing the filled sinks and development of the present-day erosion surface above, at, or below the depositional surface of the filled sinks has hampered correlation. In general, the iron-filled sinks of the south are at higher elevations than are the clay-filled sinks further north, but they occur at generally lower stratigraphic intervals. If today's topographic surface is lower than was the Pennsylvanian surface, then the iron-filled sinks of the south could conceivably have been capped by clays. The iron-bearing minerals and associated quartz may have been precipitated from the leachate of overlying clays (McQueen, 1943, p. 214-215), or they may have precipitated from fluids brought in below the filled sinks along the karst channels that drained the filled sinks (see "Proposed hypotheses for later alteration of filled-sink deposits", this report).

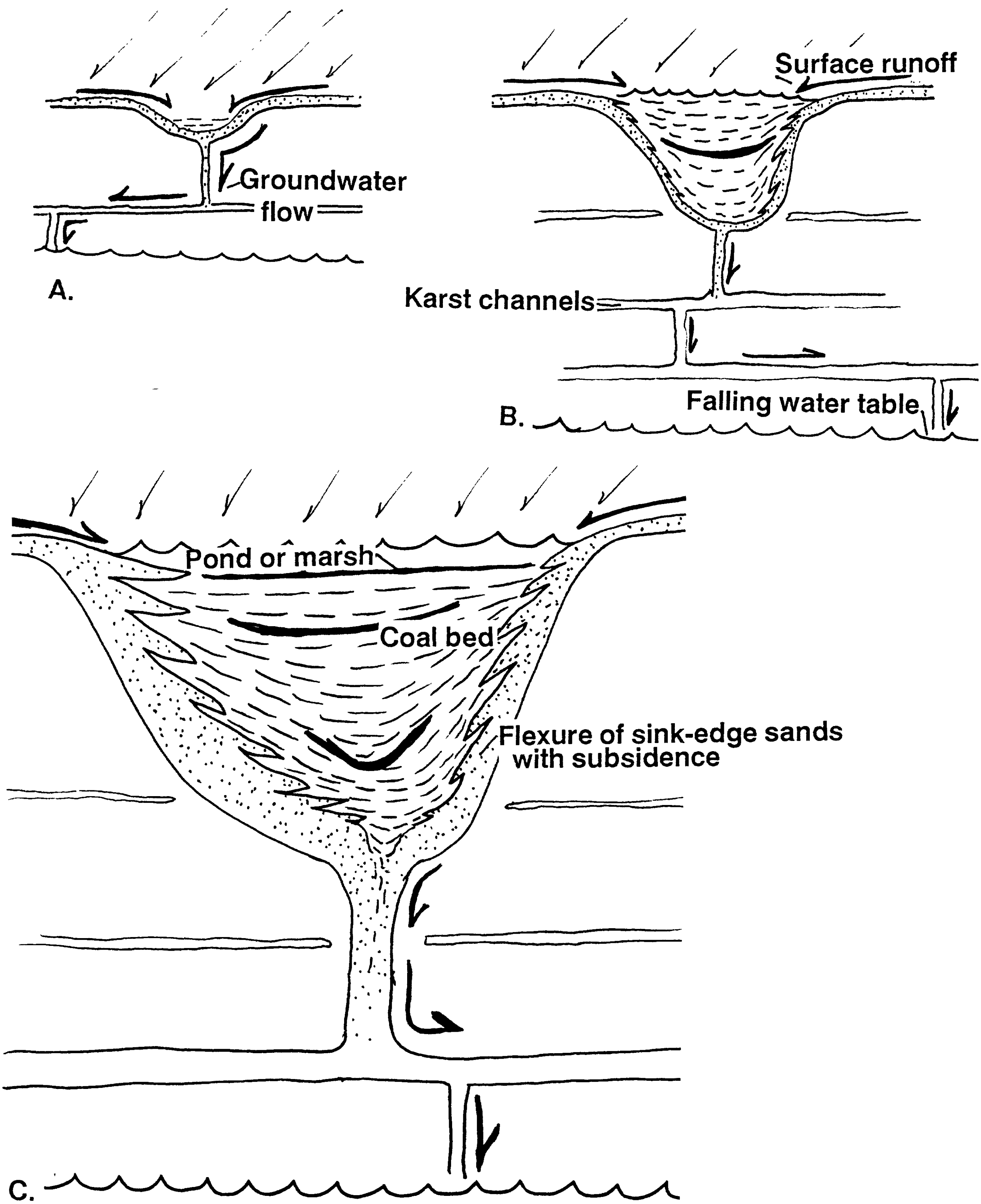

Figure 2.--Development of a filled sink.

Stratigraphy and environments of deposition of sediments associated with filled sinks

The paleotectonic settings and provenances of the Atokan Graydon and Cheltenham Formations are poorly understood because of their discontinuous subaerial deposition, the alteration process(es?) to which they have been exposed, and their subsequent post-Pennsylvanian erosion. They seem to be products of simultaneous sedimentation and subsidence in the filled-sink structures; products of intense chemical and physical weathering that were deposited on an extensive, low-lying erosional surface developed during late Mississippian and early Pennsylvanian time. In general, the Graydon Formation represents a residuum of chert and sand chemically weathered from subaerially exposed cherty dolomites and associated sands and shales. The more quartzose sandstones to the south may have been reworked from Cambrian and Ordovician sandstones exposed on the flanks of the Ozarks (McQueen, 1943). The Graydon's exact depositional relationship to the rim rock sandstones of the filled sinks remains largely unknown due to post-Pennsylvanian erosion of the surfaces where the blanketing Graydon residuum may have interfingered with, or may have been continuous with, the steeply dipping rim rock at the Pennsylvanian surface.

The Cheltenham Formation in the filled-sink region is composed primarily of claystone with subordinate amounts of sandstone and chert conglomerate and rubble. The coarser lithologies are characteristically interbedded at the edges of the filled sinks near the rim rock. The Cheltenham "lies above beds whose ages range from Ordovician to Mississippian and below Pennsylvanian strata which range in age from Atokan to latest pre-Marmaton." (p. 79, Searight and Howe *in* Howe and Koenig, 1961) Thin coals are present in some filled sinks, oriented from nearly horizontal to vertical, and *Stigmaria* and other root impressions have been found in the clays underlying the coal beds (Searight and Howe *in* Howe and Koenig, 1961). "The refractory clays, including diaspore clays, were derived from the fine insoluble residues of a surface regolith and formed lateritic soils in the probably tropical climate" (Wanless, 1975, p. 99). These residues were apparently washed into down-dropping sinks open to the surface during Atokan time, and swamp deposits of coal accumulated in some filled sinks where subsidence exceeded deposition of clastic detritus. South of the Missouri River, Pennsylvanian marine limestones have been reported above the Cheltenham claystones in some filled sinks (A.W. Rueff, oral commun., 1990)

Related karst features

In addition to filled sinks, many of the Paleozoic rocks that enclose the sinks show evidence of solution. The quandary of deformed, attenuated, and thickened sandstones and shales exposed on Cave Hill (Bretz, 1950; Westcott and others, 1973), the more subtle evidences of incipient downward solution and fill shown in figure 3 in the Jefferson City Formation near Mount Sterling, and the abundant chert and stylolites in the enclosing rocks around filled sinks suggest that a continuum of degrees and types of dissolution have been at work since the rocks' exposure to the surface in later Pennsylvanian time. Filled sinks may only be the most economic, and thus, well-exposed, member of the continuum.

Figure 3.--Downward solution of Jefferson City-Cotter Formation east of Mount Sterling, Missouri.

If the filled sinks commonly within the Canadian series Roubidoux and overlying Jefferson City-Cotter Formations represent solutional features, it is logical to consider where waters from the vadose zone and their dissolved load went below the base of the filled sink. Bretz (1956) described the caves of Missouri on a county-by-county basis and provided localities to the quarter-section or closer. If one locates Bretz' caves on McQueen's 1943 map of Missouri fire clay districts (plate 1, this report), it becomes apparent that, with few exceptions at the edge of the southern district, caves ring, and underlie, the fire clay district. Bretz (1956) states that the entrances to several caves are "developed at the contact of the Roubidoux and Gasconade formations", "in the upper beds of the Gasconade dolomite about 10 feet below the bottom of the Roubidoux sandstone", "in the Gasconade dolomite about 25 feet below the base of the overlying Roubidoux sandstone", and "60 feet below the basal sandstone of the Roubidoux."

Inspection of the Sullivan, Missouri 1:100,000 topographic map shows that the filled-sink region is developed on a relatively undissected topographic high, or plateau, between the drainages of the Meramec and Gasconade Rivers. It is along those river drainages, below the plateau on which the filled sinks are located, that most cave entrances are located. As the Gasconade underlies the Roubidoux (Howe and Koenig, 1961), the two Gasconade sandstone bodies that lie at or near the base of the Roubidoux may have served as aquifers in Pennsylvanian time, bringing ground waters down the Ozark dome. These aquifers could have hastened the development of karstic channels in the Gasconade. It may be reasonable to infer that waters that entered the filled sinks were carried away by a Pennsylvanian-age system of karstic channels, perhaps a precursor to those that now traverse units stratigraphically lower than those intersected by the filled sinks.

Precambrian terrane underlying filled-sink region

Portions of Osage, Callaway, Phelps, and Montgomery Counties are underlain by Precambrian St. Francois Terrane, and Gasconade, Franklin, and Crawford Counties are entirely, or almost entirely underlain by those units. 1.5-billion-year-old St. Francois Terrane rocks are volcanic flows and intrusives, ash-flow tuffs, and subvolcanic massifs, many of granitic composition (Kisvarsanyi, 1979). The youngest two-mica granites which lie below the filled-sink terrane contain as much as 418 ppm Li and 18 ppm U (Kisvarsanyi, 1981). Kisvarsanyi (1975, 1984) shows that the area of the filled sinks is intersected by one of Missouri's principal northwest-trending tectonic zones; that the maximum relief of the Precambrian terrane is at sea level (maximum elevation of today's surface is about 900 feet (275 m) above sea level); and that the zone is intersected by northwest-trending basement faults.

Diagenesis of filled-sink deposits

Evidence of abundant vegetation--coal beds, carbonaceous detritus and muds in the Atokan Graydon and Cheltenham Formations (McQueen, 1943)--suggests that the exposed Paleozoic aquifers higher on the flanks of the Ozark dome could have transmitted organic acids downdip to the locale of the filled sinks. In addition Missouri filled-sink deposits were exposed to the deep tropical weathering and laterizing processes typical of subaerial exposure near the paleoequator during Pennsylvanian time (Nicholas and Bildgen, 1979). The flint clay, diaspore, and böhmite, and the distribution of those minerals within filled sinks, are strikingly similar to those referred to in Valeton (1972) as kaolinites and bauxites in karst sinks of several ages and geographic areas. As in the filled sinks of Missouri, the highest Al_2O_3 and lowest SiO_2 values of karst bauxites worldwide tend to occur in the central parts of the sinkholes "where drainage was at its maximum" (Valeton, 1972, p. 168). The presence of flint clay, burley, and(or) diaspore may indicate the degree of laterization a particular filled sink underwent. Local variations in altitude above the water table, size of catchment basin, degree of opening at the bottom of the sink, and the Eh and pH of the downflowing fluids determined the final product of diagenesis, which varied across the ever-widening subaerially exposed Pennsylvanian surface.

However, the sinks to the south filled with pyrite and(or) marcasite and hematite do not fit this model. If one also plots the localities of Crane's (1912) "Hematites of the Filled Sinks" on the flint clay map in McQueen (1943) (plate 1, this report), and compares their distribution with the distribution of Cambrian and Ordovician rocks from the state geologic map (Anderson and others, 1979), one can see that hematite- (and pyrite-) filled sinks occupy both the southernmost extent (more than 15 km south of Rolla) and the oldest rocks. These facts combine to suggest that the iron-filled sinks were deeper features that formed higher on the Ozark dome than did the clay-filled sinks. The iron-filled sinks' tops may have extended well above the present topographic surface, and the sinks may have dissolved much deeper into older surrounding rocks with the drop in regional water table related to sea-level drop.

PROPOSED HYPOTHESES FOR LATER ALTERATION OF FILLED-SINK SEDIMENTS

At present there is little incontrovertible data to prove that alteration of the contents and rim rocks of the filled sinks, beyond that of normal diagenesis (lithification, desilication, laterization, oxidation), has occurred. However, in addition to their occurrence in laterized terranes, böhmite (AlO·OH) and its dimorph diaspore are also associated with metamorphosed limestones, chloritic schists, altered igneous rocks, supergene kaolin and gibbsite, and hydrothermal products of pegmatites related to alkaline igneous rocks (Roberts and others, 1974).

Although both pyrite and marcasite form under a wide variety of conditions--from pyrite in high-temperature vein deposits to marcasite from low-temperature acidic solutions associated with the deposition of clays, shales, and coal--both sulfides are also associated with mineralization of the Pb-Zn-Cu Mississippi Valley-type (MVT) deposits 30-50 km to the southeast. In 1926 W.A. Tarr suggested hydrothermal alteration of the Missouri clay deposits, after their deposition in "solution cavities" (notes reproduced in Keller and others, 1954, p. 33), mentioning the association of pyrite with the clays. In 1937 Tarr further expanded on his ideas, discussing the later exothermic oxidation of pyrite and marcasite to hematite, and its possible effect on the sandstone rim rock. Tourtelot and others (1988) suggested that some filled-sink deposits may have been hydrothermally altered by fluids with the same source of sulfur as MVT deposits, at a time coincident with MVT formation. Tourtelot and others (1990) reported, on the basis of examination of cores through, and adjacent to, a clay deposit, that a "sandstone, 120 ft thick, is variably iron stained, silica cemented, and leached, and the bedding is much disturbed. Beneath the sandstone, about 30 ft of hard, silica-cemented breccia containing pieces of limestone and chert was drilled." They stated that "These data do not contradict the hypothesis of relationship of sinkhole deposits to a regional hydrothermal event, but much more needs to be learned." M.B. Goldhaber (oral commun., 1990) suggested that sulfide-containing fluids from the southwest related to MVT fluids may have altered the hematite-and-clay fill of the southern part of the filled-sink zone, reducing the hematite to pyrite and marcasite. If such fluids were part of MVT events, and if alteration was indeed Middle to Late Pennsylvanian in age (Filipek, 1986), Atokan-age filled-sink deposits would have been in place. These fluids may have travelled along the karst passages below, and connected to, the filled sinks, rising into the filled sinks as elevation dropped to the north down the Ozark dome.

Less well-constrained in origin or time are occurrences of dioctahedral chlorite resembling cookeite ($LiAl_4(Si_3Al)O_{10}(OH)_8$) in zones of some flint clays, often near the rim rock. This mineral contains relatively large amounts of a soluble alkali metal, lithium. If, however, flint clays, diaspore, and böhmite result solely from desilication and acid leaching in the filled sinks, how is it possible that a lithium-rich chlorite (cookeite?) remains in the sink fill? Elsewhere, cookeite is associated with hydrothermal veins and lithium-rich granite pegmatites. Likewise, uranium-bearing torbernite is generally associated with pegmatites, vein deposits, and sedimentary rocks. Metatorbernite "occurs chiefly as a secondary mineral in the oxidized portion of veins or other deposits containing uraninite together with copper-containing minerals, and possibly as a low-temperature hydrothermal mineral in vein deposits" (Roberts and others, 1974). The buried, basement-faulted topographic highs of Precambrian rhyolitic tuffs and two-mica and alkali granites beneath the filled-sink district may have directed hydrothermal fluids containing uranium, copper, and lithium upward along preexisting karst solution features. The resultant uranium, copper, and lithium minerals were deposited near the borders of filled-sink deposits.

In summary, two events may have led to the development of filled sinks that now contain arguably high-temperature minerals. First, vertical dissolution of the host rock occurred, creating sinks open to the surface on the low-lying coast of the retreating Atokan-age sea. Low-energy fluvial and paludal sedimentation largely kept pace with continued subsidence of the sinks as the sea retreated. Contemporaneous with dissolution and infilling, or shortly thereafter, leaching and desilication of the sink fill by organic-acid-rich surface and shallow ground waters occurred. Thus, kaolinitic and bauxitic deposits characteristic of the wet, warm Pennsylvanian climate developed in a karst setting. Those same karst features may have served later as conduits for upward movement of hydrothermal(?) fluids possibly related to MVT deposits, and(or) that had been in contact with underlying alkalic and silicic Precambrian igneous rocks. Thus was deposited a lithium-rich chlorite uncharacteristic of desilication and acid leaching in some filled-sink deposits.

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