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Chapter 8

A Discussion of Flow Mechanisms Responsible for Alteration and Mineralization in the Cambrian Aquifers of the Ouachita-Arkoma Basin-Ozark System

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ABSTRACT

Cathodoluminescent microstratigraphy in epigenetic dolomite cements correlates over a north-south distance of >275 km across the Ozark Mountains. Trace elements in dolomite show coherent regional variations. Ubiquitous coeval Pb-Zn mineralization contains fluid inclusions with homogenization temperatures >100°C. All suggest the flow of brines (mainly) north from the Arkoma Basin through Cambrian sandstone and carbonate aquifers. The observation that brines still fill Ordovician and Cambrian strata ringing the Ozark Plateau constrains the cumulative flow that has occurred. If the Mid-Continent sediment cover was thick and insulating, brine flow driven by topographic differences in hydrologic head could have been slow enough to avoid salt flushing and still accommodate the fluid inclusion homogenization data. If the cover was thermally conductive and thin, as seems most geologically reasonable, flow at the rates required to explain the homogenization temperatures would have quickly flushed salt from the aquifers in contradiction to present observations. Topographically driven hydrologic flow across the Arkoma basin could not have continued uninterrupted for protracted periods. Given the present high permeability of the Pb-Zn deposits, there is no obvious way to limit or pulse cross-basin hydrologic flow. The simplest explanation is that brines were expelled by compaction or gas displacement. High temperature, low salinity fluid inclusions in the Ozark Cambrian aquifers probably represent the incursion of meteoric water into outcrop areas warmed by pulses of brine outflow. Channeling of fluid flow and the relation of alteration and fluid inclusions to flow channels need to be further investigated theoretically and in the field.

INTRODUCTION

The flow of brine north from the Arkoma Basin has produced remarkably extensive and coherent alteration in Upper Cambrian sediments across Arkansas, Missouri, eastern Kansas, and eastern Oklahoma (Figure 1). The alteration includes: (1) A correlatable cathodoluminescent microstratigraphy in hydrothermal epigenetic dolomite cements over a N-S distance of ~275 km (Figure 1B; Voss and Hagni, 1985; Rowan, 1986; Farr, 1989), (2) almost ubiquitous traces of Pb-Zn mineralization coeval with deposition of the dolomite cement (Voss et al., 1989; Coveny et al., 1987), and four or more major Mississippi Valley-type (MVT) Pb-Zn mining districts, (3) fluid inclusion homogenization temperatures in four mining districts that range from 60 to 180 °C (Leach and Rowan, 1986; Rowan and Leach, 1989), (4) a northward increase in K/Cl in fluid inclusions with constant Na/Cl ratios (Viets and Leach, 1990), and (5) a regular northward decrease in Fe, Mn and $^{87}Sr/^{86}Sr$, and an increase in the Sr contents of epigenetic dolomite within 1 m of the Lamotte Sandstone contact (Gregg and Shelton, 1989a, b). Carbon and oxygen isotopic ratios in the epigenetic dolomites vary in a fashion consistent with thermal excursion(s) from 50° up to 130° and then back to 50°C (Gregg and Shelton, 1989a). The spread in fluid inclusion homogenization temperatures, banding and dissolution in the dolomite cement stratigraphy, episodes of metal deposition with dissolution in between (Sverjensky, 1981; Hagni, 1976), and the wide range of lead isotopic ratios in single galena crystals (Hagni, 1976; Hart et al., 1981) indicate variable physical or chemical conditions. Structural control of brine flow from the Arkoma Basin by the Reelfoot Rift (Farr, 1989) and brine flow south from the Illinois Basin (Gregg and Shelton, 1989b) are suggested by the pattern of trace elements in the dolomite cements. The Ozark-Arkoma system is similar in many respects to other basin margin systems, especially for example the Marathon-Permian Basin-Llano uplift, the Western Canada Basin, and the Appalachian basin, all of which host MVT lead-zinc deposits.

Two flow mechanisms are generally considered possible explanations for the MVT lead-zinc deposits and their associated epigenetic alteration: Bethke (1986); Bethke et al. (1988); and Garven (1984, 1985) proposed that MVT deposits are produced when basin brines are moved out of a basin by gravity flow from highland areas such as the Ouachita mountains. This hypothesis is favored by many for the Ozark Mountains (e.g., Leach and Rowan, 1986) because the mineralization and alteration found there require the throughput of large fluid volumes. Given enough time, gravity flow can propel almost unlimited quantities of fluid. The other flow mechanism that has been suggested for MVT deposits and their associated alteration is the expulsion of brines by compaction or processes related to sediment heating such as gas generation and water displacement from accumulating and deforming sediment piles (Sharp, 1978; Cathles and Smith, 1983; Oliver, 1986; Rich, 1927). The volume of brine that can be expelled by these mechanisms is limited but adequate to produce the observed mineralization and alteration. The purpose of this chapter is to examine these competing mechanisms of fluid flow with reference to the alteration and mineralization in the Ouachita-Arkoma Basin-Ozark system.

THE OUACHITA-ARKOMA BASIN-OZARK SYSTEM

The flow system considered in this paper is shown in Figure 1. What is today the Ouachita orogenic belt was a rifted Atlantic-type margin in early and middle Paleozoic time (Houseknecht,1986; Arbentz; 1989). The 0–150-m-thick, quartzose Lamotte sandstone was laid down unconformably on Precambrian basement and covered by shallow marine carbonates and shales from Cambrian to Early Pennsylvanian time. The maximum thickness of these strata is 1.5 km. Overthrusting from the south in Pennsylvanian time flexed the margin down to form a classic foreland basin. Sedimentation increased abruptly at ~310 Ma (Arbenz, 1989, figure 7). Five and a half kilometers of Atokan sediments were deposited in just 5 m.y. Portions of these and earlier marine sediments were thickened tectonically as they were caught up in the Ouachita thrusting and folding. The deformation and sedimentation ceased shortly after Atokan time.

The Cambrian and Ordovician stratigraphy of the area is shown in Figure 2. From a diagenesis–fluid-flow perspective, perhaps the most remarkable aspect of the transect shown in Figure 1 is the continuity of the microstratigraphy displayed by epigenetic dolomite in the Upper Cambrian to basal Atokan units. The Lamotte Sandstone appears to have been the main conduit for the flow of mineralizing brines, although brines also moved through the overlying Cambrian dolomites and underlying granitic basement. Hydrothermal dolomite cements in these strata have a characteristic cathodoluminescent banding. As indicated in Figure 1B, hydrothermal dolomite banding and cement dissolution events can be correlated over the ~70-km-long Viburnum Trend (Voss and Hagni, 1985), between the Viburnum Trend and the Northern Arkansas Pb-Zn district (Rowan, 1986), and for 70 km or so north and west of the Viburnum Trend (Farr, 1989; Voss et al., 1989; Gregg, 1985), a distance of at least 275 km along this section.

The nature of the cathodoluminescent banding varies systematically. The number and intensity of bands increases abruptly near the Bonneterre-Lamotte transition and then decrease upward with much

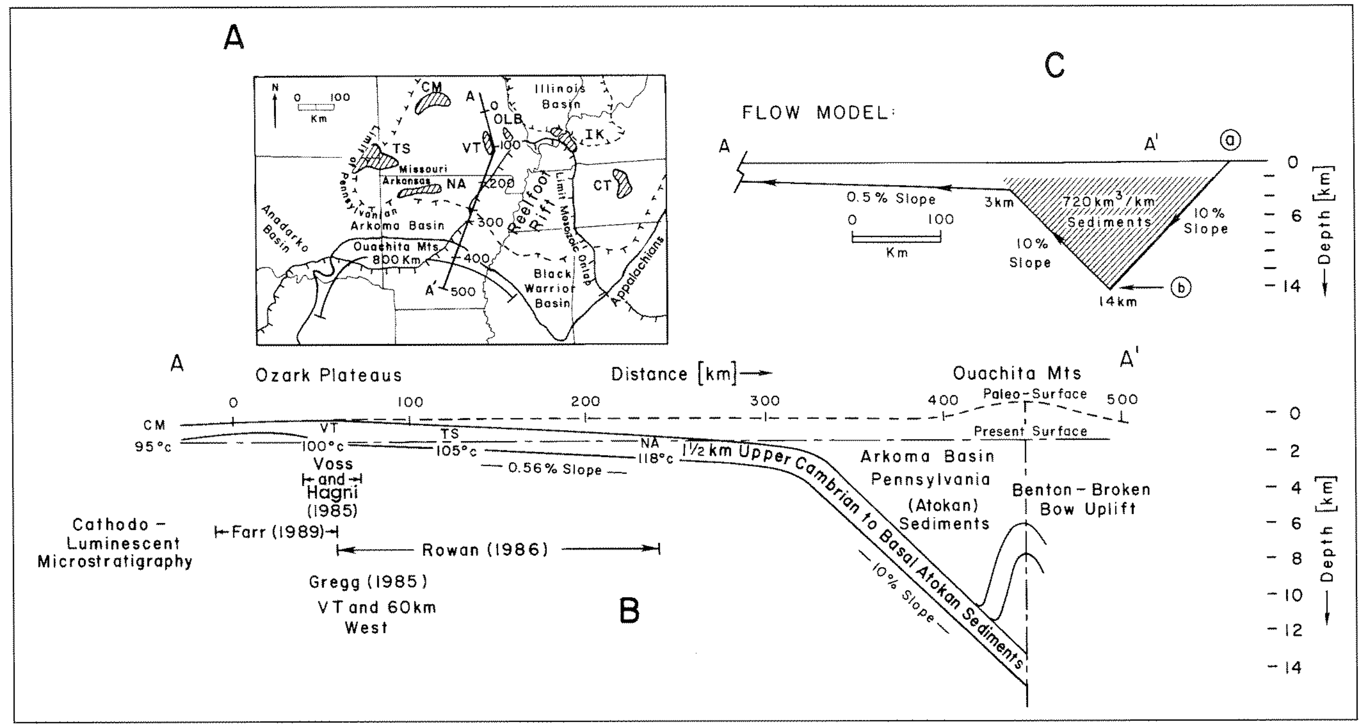

Figure 1. Mississippi Valley-type Pb-Zn (MVT) districts (A) and the continuity of the cathodoluminescent microstratigraphy in hydrothermal dolomite cements in the Mid-Continent (B) are shown in relation to the subsurface geology (B). The base map (A) is after Houseknecht (1986, Figure 1). The cross section (B) is constructed from sections in Thacker and Anderson (1977), Houseknecht (1986), and Arbenz (1989). MVT districts are after Viets and Leach (1990, figure 1) and are labeled: CM= Central Missouri, VT=Viburnum Trend, OLB=Old Lead Belt, NA=Northern Arkansas, IK=Illinois-Kentucky, CT=Central Tennessee, TS=Tri-State. The flow paths used in the calculations presented in Figure 5 are labeled in (C).

fewer and lower intensity bands in shale units (Farr, 1989). These relationships are expected because: (1) iron above a certain concentration inhibits luminescence, (2) Fe and Mn (the main fluorescent agent) are consumed by dolomitization, and (3) shale inhibits fluid throughput and therefore alteration (Farr, 1989). In the middle and lower Bonneterre the number of bands and the percentage of dull bands increase from the St. Francois Mountains (which lie between the Viburnum Trend (VT) and Old Lead Belt (OLB) districts in Figure 1A) to both the south and east. This is consistent with relatively Fe- and Mn-rich brines reaching the St. Francois Mountain area both by flowing directly north out of the Arkoma and by flowing from the Arkoma northeast along the Reelfoot Rift and then east along the northwest striking Broomfield Lineament that connects the Reelfoot with the St. Francois Mountains area. Deposition of distinct sulfide minerals occurs district wide between particular cathodoluminescent zones (Voss et al., 1989).

An excellent and comprehensive review of all aspects of the chemical and isotopic alteration of the area that supports and augments the inferences drawn from the dolomite cement microstratigraphy has been given by Gregg and Shelton (1989a). Trace elements in the hydrothermal dolomite within 1 m of the Bonneterre-Lamotte transition show an increase in Fe and Mn and a decrease in Sr from the St. Francois Mountains to the south (Gregg and Shelton, 1989b). The pattern is absent 3 to 6 m above the contact, however, indicating less flow in that part of the Bonneterre. Similar Fe, Mn, and Sr trends from the St. Francois Mountains to the northeast suggests that brines arrived in the same cathodoluminescent time-bracket from the north. Flow from the Illinois Basin as well as from the Arkoma basin seems to have contributed to alteration and mineralization (Gregg and Shelton, 1989a,b). The decrease in Fe and Mn upward in the Bonneterre from the Lamotte sandstone, as well as Mn, Fe, Zn, Na, and K enrichment in shales higher in the stratigraphy, suggest that mineralizing fluids upwelled from the Lamotte and Bonneterre in the Viburnum trend area (Gregg and Shelton, 1989a). Detailed study of the concentration of these elements in the most fractured parts of shales above the Buick mine, where upward leakage was perhaps greatest, show that enrichment of Na, Mn, Fe and Zn was followed by depletion to background levels (Panno et al., 1988). Depletion did not occur in the less fractured parts of the shale. The leaching of the fractured parts of the shales may be related to the dissolution of sulfides and hydrothermal dolomite in the ore zones;

both could be caused by meteoric inflow.

As shown in Figure 3, fluid-inclusion homogenization temperatures from different mining districts in the region range from 60° to 180°C. Fluid inclusions in baroque dolomite in the upper Bonneterre formation in the Reelfoot Rift suggest two much hotter episodes of heating, the first with mean homogenization temperatures of 235°C and the second with mean temperatures of 170°C (Tobin, 1991). Fluid inclusions in the core of the Ouachita Mountains have even higher homogenization temperatures up to 300°C (Shelton et al., 1986). A general decrease in temperature across the ore district is suggested by these data, especially if flow was directed from the Reelfoot rift, and the Ouachita homogenization temperatures are indicative of the temperatures of fluids entering the Cambrian aquifers at the base of this sediment pile.

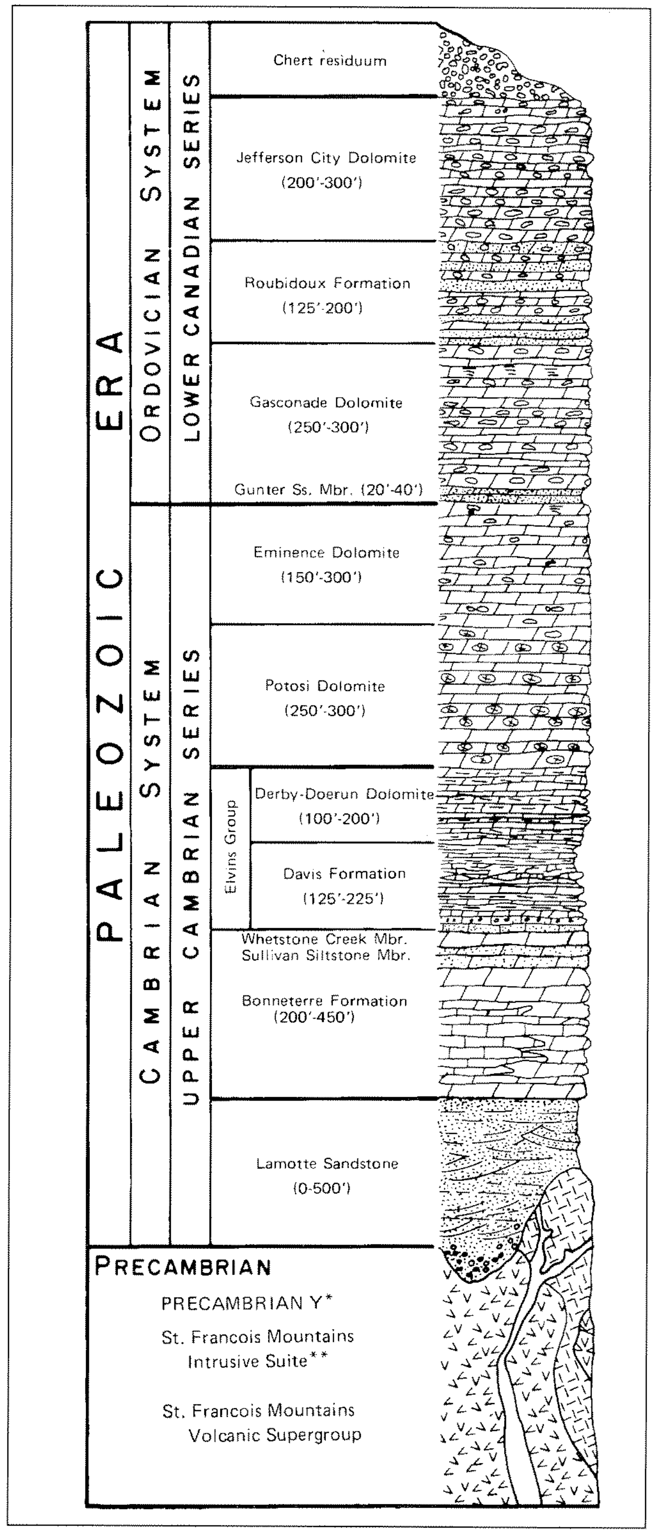

Figure 2. Paleozoic stratigraphy in the St. Francois Mountains area from Kisvarsanyi (1976, p. 2).

There is a large scatter in the homogenization data from the mining districts in Missouri and Arkansas, however, and the scatter is far bigger than the difference in modal temperature between districts. Leach and Rowan (1986) attribute this to inclusion necking, but it could also reflect real temperature variations associated with pulsing flow. The reality of the modal trend of 0.09°C/km they deduce from the mining district data in Figure 3 could certainly be questioned (e.g., Gregg and Shelton, 1989a; Shelton et al., 1992), and for this reason the line connecting the modal data drawn in Leach and Rowan's original figure has been omitted. There is a general consensus that the sites of ore deposition were never buried by more than 1 to 1.5 km of sediment. Mineralized areas seem therefore to have been at temperatures considerably above those that would be predicted by their burial depths at the time of mineralization. This is the most significant point shown by Figure 3. Almost everyone attributes this thermal elevation to fluid flow in the Lamotte and other Cambrian aquifers.

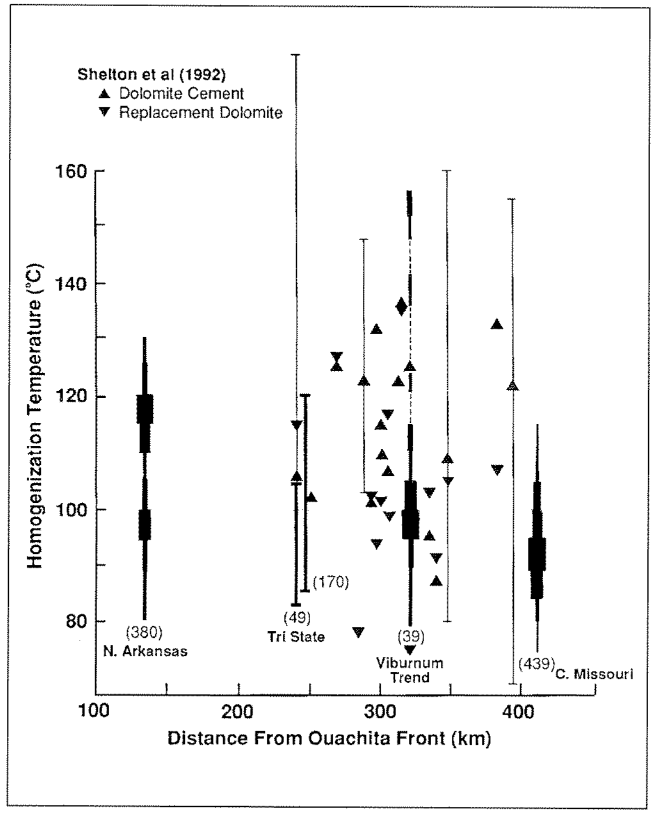

Figure 3. Homogenization temperatures of fluid inclusions in sphalerite from some of the mining districts shown in Figure 1, and in epigenetic dolomite from the Bonneterre (Cambrian) aquifers in southeastern Missouri. Mining district data are from Leach and Rowan (1986) and are indicated by heavy lines or boxes. The width of box indicates number of inclusions homogenizing within the temperature range indicated by the length of the box. The dolomite inclusion data cover the area indicated by the dashed box in Figure 4 and are from Shelton et al. (1992).

The present-day flow system in the Ozark area is an interesting one. Water recharges and flows radially out from the Ozark Plateau through Cambrian to Mississippian strata, labeled upper Cambrian to basal Atokan sediments in Figure 1B and known hydrologically as the Ozark Plateaus Aquifer System (Jorgensen et al., 1988). At the same time, flow sweeps east through the deep Western Interior Plains Aquifer System from catchments in the Front Range of the Rocky Mountains, picks up salt in Kansas, and upwells where it meets the outward flowing waters of the Ozark Plateaus Aquifer System (Jorgensen et al., 1988; Banner et al., 1989). One of the brine springs that express this upwelling is "old Boonslick" where Daniel Boone "settled and manufactured salt" (Figure 4) (see Shepard, 1907, p 78). Where strata carrying the eastward-moving waters approach the surface in eastern Kansas and Oklahoma, the surface temperature gradient is increased to ~40°C km^{-1} (Stavnes and Steeples, 1982; Luza et al., 1984).

It is important to recognize that basin brines today occupy the deeper parts of the Cambrian aquifers and almost completely ring the Ozark Plateau. This is shown clearly in recent maps by Jorgensen et al. (1986) and older maps published by Dott and Ginter (1930). Data from these sources are summarized in Figure 4. As stated by Dott and Ginter, "The most striking feature of the map [Figure 4] is the seeming relationship between the concentration of [Cambrian and] Ordovician waters [e.g., waters contained in Cambrian and Ordovician strata] and outcrops of Ordovician rocks." Equivalent fresh water head maps make it clear that the reason for this relationship is that fresh waters recharging outcrop areas such as the Ozark Plateau have, over time, swept out the brine (Jorgensen et al., 1986). Present-day flow directions inferred from the contours in equivalent fresh water head are shown by arrows in Figure 4. Meteoric recharge has not swept brines from the same aquifers deeper in the Illinois, Arkoma, and Oklahoma basins. In fact the flow from the Ozark Plateau meets the flow from the Rocky Mountains in the areas of present brine upwelling (Jorgensen et al., 1986).

The geology and geochemistry reviewed above indicate that starting in Permian time, basin brines moved, perhaps in pulses, from the Arkoma basin (and other basins) through the Lamotte Sandstone and other Cambrian strata to Mississippian aquifers and produced regional, coherent chemical and isotopic alteration and extensive lead-zinc mineralization. Rich deposits of lead and zinc accumulated where the aquifers cropped out (e.g., the St. Francois Mountain area), were cut by permeable units (e.g., the reefs of the Viburnum Trend), or where they were intensely fractured. Meteoric water enters these same outcrop areas today, and brine has been displaced by fresh water. This may also have occurred in the past, in between pulses of brine outflow. At the same time there is today a regional cross-basin hydrologic flow system carrying waters from the Rocky Mountains to Kansas and Missouri, and this flow is expelling brines in salt springs such as old Boonslick. The present-day Mid-Continent thus provides a good backdrop for discussing the nature of the brine flow that occurred there in the past and produced extensive and coherent alteration and mineralization.

THERMAL CONSTRAINTS ON FLUID FLOW

Both cross-basin hydrologic flow and basin dewatering must produce flows sufficient to explain the fluid inclusion homogenization temperatures in Figure 3. We start with an analysis of this thermal constraint following the approach developed by Cathles and Smith (1983). We ask the simple question: How fast must waters flow out of the Arkoma Basin to heat the Cambrian aquifers in the Ozarks to temperatures of 80° to 120°C? The critical issue is the heating of the aquifer system. If the aquifer has the required temperatures, fluids will be able to move locally upward in fractures or permeable cross-cutting strata and deposit minerals with little loss in temperature, recording the aquifer temperatures as they do so. If the aquifer system is not heated sufficiently, local fluid upwelling at any rate will not be able to produce fluid inclusions with the required homogenization temperatures. To put the problem in a present-day context, temperatures in the Arbuckle or Rice aquifers in Kansas would need to be 80° to 120°C at ~1 km depth. They are ~40°C (25° to 30°C above ambient) at this depth today. Weak flow through these aquifers elevates the thermal gradient near where the aquifers crop out to ~40°C km^{-1}, but these gradients do not extend to depth. Much greater flow rates would be required to bring waters of 80° to 120°C within a kilometer of the surface.

How much faster the flow must have been to accommodate the temperatures and depths thought to have existed during Pb-Zn mineral deposition in Missouri and Arkansas can be determined by calculating the temperature profile in a basal aquifer or

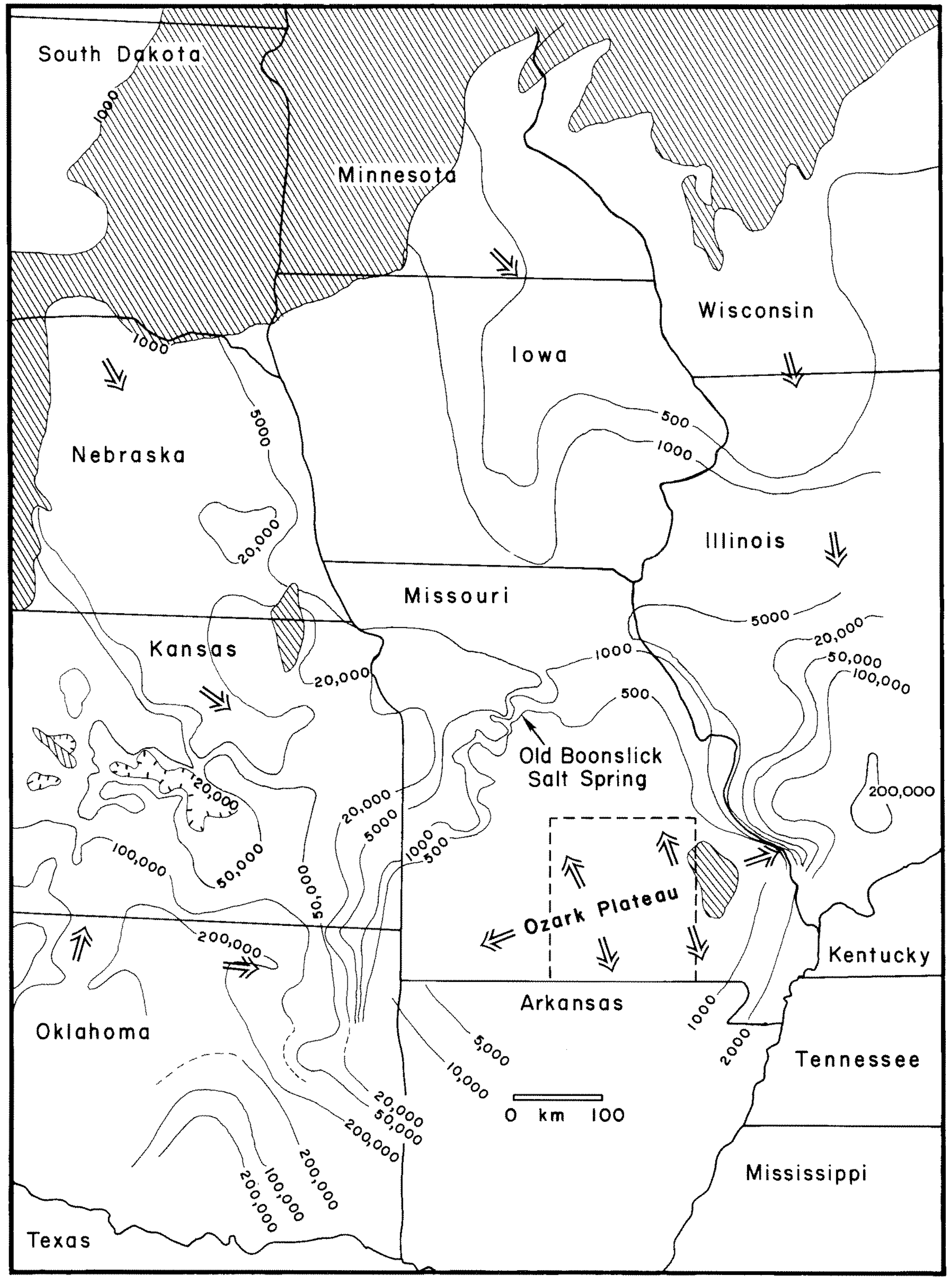

Figure 4. Dissolved solids concentration (ppm) in Cambrian and Ordovician sediments in the Mid-Continent area from Jorgensen et al. (1986) and, in southern Oklahoma, Arkansas, and southeastern Missouri, from Dott and Ginter (1930). Present directions of fluid flow, inferred from contours of fresh water equivalent head given by Jorgensen et al. (1986), are shown by arrows. Arrow length has no significance. Present day flow originates from areas where Cambrian and Ordovician sediments outcrop (hachured areas) or nearly outcrop. This flow has flushed brines from the Cambrian and Ordovician strata as shown in the figure and discussed in the text. The dashed box indicates the area where detailed studies of drill core fluid inclusions and alteration have been carried out by Gregg, Shelton, and others.

aquifer system by daisy-chaining analytical solutions for steady state temperatures along aquifer segments of uniform dip (Cathles, 1987). Analytical solutions for each linear (uniform dip) segment of the aquifer are joined together by requiring continuity of flow and temperature. The temperature at only one location along the aquifer need be specified. The temperature profile then depends on the thermal conductivity, K, of the sediments above the aquifer, the regional heat flow, j_o, and the total flow per unit strike length through the aquifer or aquifer system, Q.

Both j_o and K are parameters of critical importance, especially in the flat portion of the flow path across the Ozark plateaus. The Cambrian to Mississippian cover in this area consists today of a basal sandstone overlain by carbonates with some shales. In the St. Francois Mountains area, this stratigraphy is ~80% carbonate, ~12% sandstone, and ~8% shale (Figure 2). The thermal conductivity of a lithologic sequence can be estimated using the porosity-dependent rock type thermal conductivities and porosity-depth relations in Royden and Keen (1980). I calculate using Royden and Keen's relations that the effective thermal conductivity of a 2.5-km-thick column of sediment consisting of 80% carbonate, 12% sandstone, and 8% shale is ~5.6×10^{-3} cal/cm-s-°C (5.6 Thermal Conductivity Units, or TCU). Without compaction, the thermal conductivity would be ~5 TCU. The column would have to be 53% shale to have a thermal conductivity of ~4 TCU. If the sediments now eroded from the Ozark plateaus were dominantly shale, a value as low as ~4 TCU might be approached. It is more likely, however, that these shallow water sediments would have been sands or carbonates, in which case the effective thermal conductivity of a 2.5 km section would have been between ~5.6 TCU (all carbonates) and ~6.5 TCU (50% carbonates, 50% sand). A lower bound for the thermal conductivity of the sediments covering the Ozark plateaus at the time of brine movement is therefore probably ~4 TCU and the most reasonable estimate ~5.6 TCU or greater. Heat flow in Missouri today is ~1.3×10^{-6} cal/cm^2-s or 1.3 Heat Flow Units (HFU; Kron and Stix, 1982). There is no reason for it to have been significantly different in Permian time.

Figure 5 shows the thermal profile along the "Cambrian aquifer loop" produced by cross-basin flow of various magnitudes. In Figure 5A, K=5.6 TCU, j_o= 1.3 HFU, and Q[cm^3/cm-s] is specified in terms of the dimensionless parameter α, where $\alpha = K/Q\ c \tan \beta$, and $\tan \beta$ is the dip of the steep Ouachita-Arkoma aquifer segments (=0.1) and c is the heat capacity of water (= 1 cal/cm^3-°C). Temperatures in the Cambrian aquifers (Lamotte Sandstone, Eminence Dolomite, etc.,) are not elevated significantly at any flow rates for these parameter values. The narrow Ouachita-Arkoma Basin complex is cooled by the high flow rates (low values of α) before aquifers in the Ozarks can be significantly warmed.

Figure 5B shows that if K=4 TCU, cross-basin flow can warm the Ozark Cambrian aquifers to the levels indicated by the modal fluid inclusion homogenization data in Figure 3 in the south end of the transect near the Northern Arkansas District. However, even very large uniform flow rates cannot produce the temperature increases required by the modal (let alone maximum) fluid inclusion homogenization data in the north near the Central Missouri District. Uniform cross basin hydrologic flow thus cannot match the modal fluid inclusion temperatures over the entire Ozark transect for the depth of burial selected, even in the unlikely event that the effective thermal conductivity of the cover was as low as 4 TCU. The Ouachita-Arkoma belt is too narrow to sufficiently heat waters flowing uniformly across it at the rates that would be required to warm the margin to the levels observed.

It is important to note that if the thermal conductivity of the Ozark cover could be lowered just slightly below 4 TCU, or if the cover thickened, the requisite temperatures could be attained with very slow or no fluid flow. For example, if the effective thermal conductivity of the Ozark cover were 3 TCU and the regional heat flow 1.5 HFU, the unperturbed thermal gradient would have been 50°C/km and temperatures adequate to explain the Ozark fluid inclusion homogenization temperature data could be obtained under 1.5 to 2 km of cover with no fluid flow at all. A similar result could be obtained if the cover were substantially thicker. In either case, fluid movements could have been slow and the required Pb, Zn, Mn, etc. brought in over a protracted period of time.

If the Ozark cover were not thick and insulating, cross-basin flow could still produce the required temperatures in the Ozark aquifers if the flow were nonuniform in time or space. If the flow is sufficiently focused once it leaves the deep warm sections of the flow loop under the Ouachita Mountains and Arkoma Basin, the temperatures required by the fluid inclusion data can be attained at the Central Missouri Pb-Zn district and other distal Ozark locations. The Ouachita-Arkoma flow rates that raise the temperatures of the 3-km-deep slope break the most (to ~180°C above surface ambient) are characterized by α=~-2 (see Figure 5A). If the flow is then focused by a factor of 40, daisy-chain calculations indicate that distal locations are warmed to the extent required by the modal fluid inclusion data.

The requisite distal temperatures could also be attained by transient (pulsed) flow. Across-basin flow will initially displace deep, warm brines from the Arkoma just as will compactive or other types of basin dewatering. The initial flow of warm brine could heat the Ozark aquifers to temperatures

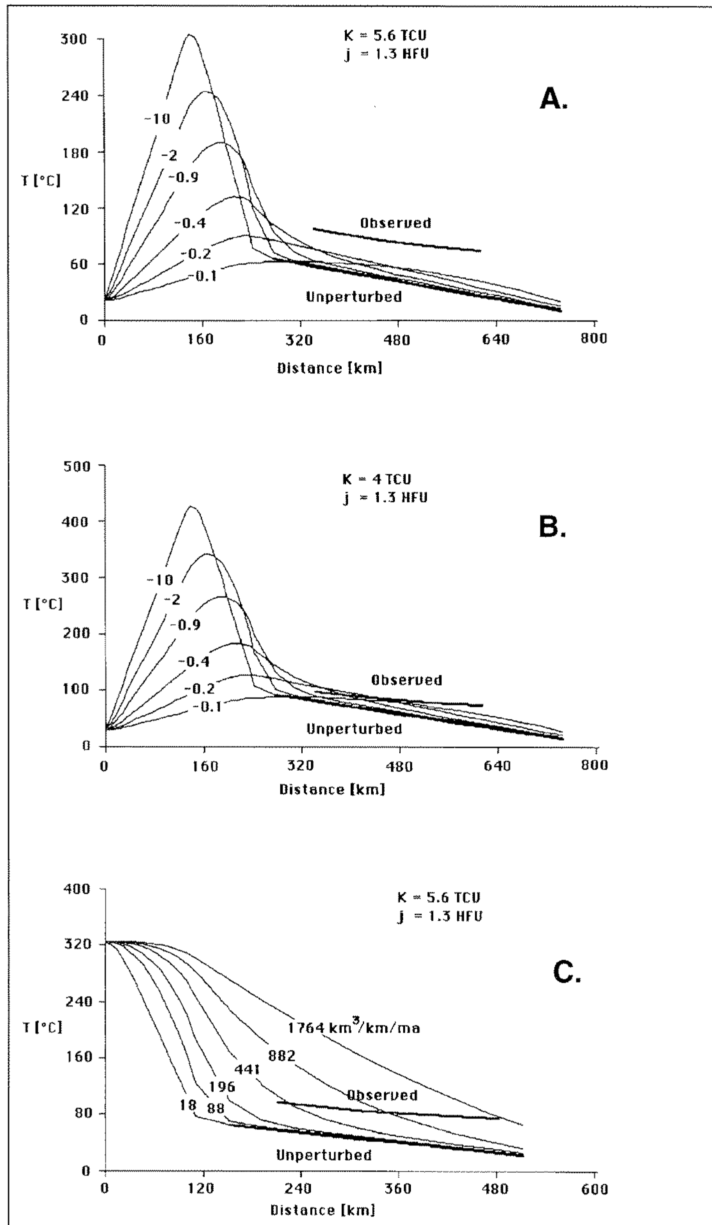

Figure 5. (A) Temperature profile in degrees Centigrade above ambient along flow path "a" (which starts at the surface in the Ouachita highlands, moves to 14 km depth, then to 3 km depth and then to discharge in Ozark plateaus as shown in Figure 1C) calculated for various values of the dimensionless flow rate parameter α. Smaller values of α indicate larger flow rates. Regional heat flow j = 1.3 x 10^{-6} cal/cm-sec or 1.3 HFU; the thermal conductivity of the cover, K=5.6 x 10^{-3} cal/cm-sec-°C or 5.6 TCU. On this and the other figures the normal unperturbed temperatures along the Cambrian aquifers are indicated by the lower heavy line labeled "unperturbed." The modal homogenization temperatures in Figure 3 with an ambient temperature of 20°C subtracted are indicated by the upper heavy line labeled "observed." (B) Temperature profiles for various values of α along loop a in Figure 1 for K= 4 TCU and j_o=1.3 HFU. (C) Temperature profile (in degrees Centigrade above ambient) along flowpath "b" (which starts at 14 km depth and then follows flowpath "a" as shown in Figure 1C) calculated for various values of α under the same conditions as Figure 5A. Fluids are assumed to enter the Cambrian aquifers at 14 km depth at equilibrium temperatures for that depth (325°C above ambient). The flow rates, Q, shown in this figure correspond to the values of α given in Figures 5A and 5B. For example α= -0.1 corresponds to Q = 1744 km^3/km/m.y. The formula relating α and Q is given in the text.

approaching those in the deepest parts of the Ouachita-Arkoma basin. With continued flow, those deep locations will be cooled by cold meteoric inflow and temperatures in the Ozark aquifers will drop. Temperatures in the Ozark aquifers will thus rise and fall in a transient fashion. The maximum transient temperatures that could be attained at various flow rates can be estimated if brine is introduced to the deep extension of the Ozark Cambrian aquifers at temperatures normal at those depths under no flow, thermal equilibrium conditions (path b in Figure 1B). Figure 5C shows that such flow can elevate temperatures in the Cambrian aquifers to the highest end of the modal ranges indicated in Figure 3. The required temperatures in the south can be produced by flow rates of 441 km^3/km/m.y. (α=-0.4). In the north, flow rates of 1764 km^3/km/m.y. (α=-0.1) are required. Temperatures in the south and north are thus compatible with a flow in the Cambrian aquifers that concentrates by a factor of 4 as it proceeds north. If the aquifers in question have a cumulative thickness of 100 m, the Darcy flow rate would have increased northward from 4.4 to 17.6 m yr^{-1}.

There is general agreement regarding the flow rate required to heat a basin margin. For example the flow rates required to significantly warm the outflow margin of the Illinois Basin (slope ~0.75%) in Bethke's (1986, Figure 11b) analysis of the Upper Mississippi Valley Pb-Zn district in Wisconsin was ~540 km^3/km/m.y. The long, flat, deep flow segment across the Illinois Basin avoids the heating problems caused by the narrowness of the Ouachita-Arkoma system and allows sufficiently warm fluids to enter the margin aquifers at the rates required. Once warm enough fluids are obtained, however, the flow rates needed to warm the margin aquifers are similar to

those we estimate. The fundamental parameter controlling margin heating is Q. My estimates of Q are minimum estimates. To the extent that flow is less concentrated in basal units, conductive thermal losses would be greater (because the heat has less distance to diffuse to the surface), and Q must be greater for the same basin margin temperature perturbation.

SALINITY CONSTRAINTS ON CUMULATIVE FLUID FLOW

Requisite flow rates of ~441 km^3/km/m.y. and the present-day pore water salinity distribution place severe constraints on how possible flow mechanisms could have operated in the Ouachita-Arkoma-Ozark area. In cross-basin hydrologic flow, fresh meteoric water will rapidly displace brines and dissolve any salt contacted. For example, if the Arkoma-Ouachita sediments contained 10 volume-% evaporites and the flow contacted these evaporites, cross-basin flow at 441 km^3/km/m.y. would dissolve and carry away all the salt in 1.25 m.y. In this calculation we assume 10% of the 720 km^3/km Ouachita-Arkoma section is salt, that salt has a density of 2 g cm^{-3}, and that the efflux has a salt-saturated salinity of 26 wt%. The salt is dissolved when the salt transported out of the basin in time t, 0.26 Q t, equals the amount of salt in the basin, 720 (0.1) (2 g cm^{-3}). If the flow rate were 88 km^3/km/m.y. (α=-2), the same amount of salt would be flushed in 6.25 m.y.

The dilemma such fast flushing of salinity poses for cross-basin hydrologic flow is as follows. Erosion is a slow process. Once the topography to "drive" cross-basin hydrologic flow is established, it will take tens of millions of years to remove. The permeability of the MVT deposits we have been discussing remains for the most part very high today. Six and a half tons of water were pumped for every ton of ore mined in the Old Lead Belt in 1943 (Weigel, 1943). Two years of pumping were required to achieve a 700 ft drawdown prior to mining in the Viburnum Trend (Bullock, 1973). Thus, although there may have been permeability reduction where metals were deposited in disseminated fashion in matrix pores (~90% of the ore is of this type; personal communication from Jay Gregg, 1992), the fracture and breccia pathways that channeled fluids to these areas remains high. The flow paths have clearly not been plugged by alteration or mineral precipitation. Also it is clear from the position of the deposits that brine discharged upward through them to the surface at the time of mineralization. Consequently it is difficult to see how brines could remain in the basins surrounding the Ouachitas if cross basin hydrologic flow at the rates required to account for the modal homogenization temperatures in MVT deposits in the area were ever established. The lack of a full (or even partial) salinity flush from the deep parts of the basins surrounding the Ozark plateaus that are thought to have produced the MVT mineralization in the region (the Illinois and Arkoma basins) appears to pose a fundamental difficulty for the cross-basin hydrologic flow model in the Ouachita-Arkoma-Ozark area and elsewhere (Cathles, 1987). Either a way must be found to turn off cross-basin hydrologic flow shortly after it is established by tectonic events, or a way must be found to explain why the basin brines have not been flushed by such flow.

Compactive dewatering does not have a salinity flush problem because fresh water does not enter the basin and only a portion of the pore waters are compactively expelled. On the other hand, as discussed by Cathles and Smith (1983), transient compactive expulsion is constrained by two kinds of heat balance considerations. If the accumulation of the 720 km^3/km of sediments shown in Figure 1C occurred in 10 m.y. (probably a generously rapid rate), for example, and caused 10% compaction, fluids would be expelled at ~7 km^3/km/m.y. This is ~1.6% of the rate required to warm the margins (441 km^3/km/m.y.) by the requisite amount. Dewatering of the Arkoma must be focused ~62 fold on the margins or temporally episodic if the dewatering model is to warm the Ozark Plateaus Aquifers as observed. Furthermore each dewatering pulse must be of sufficient volume to warm the escape aquifers. If the Cambrian Ozark aquifers cumulatively had an average thickness of 100 m over the 330 km from their bend in Figure 1B to the Central Missouri MVT District, a volume of water ~33 km^3/km would be required for each pulse. The 720 km^3/km sediment prism in Figure 1b could thus contribute about 2 pulses of fluid. If there were progressive channeling of brine flow paths to the north, which is reasonable to expect and indicated by the pattern of geochemical alteration (channeling along Reelfoot rift), more pulses could be delivered. For example, if flow were focused by a factor of four by channeling, 8 pulses of warm brine could be delivered to areas as far north as Central Missouri.

FLOW REQUIREMENTS OF MINERALIZATION AND ALTERATION

The limited quantities of brine that might be compactively expelled from the Ouachita-Arkoma system are adequate to produce the mineralization and alteration observed in Arkansas and Missouri. If we take the axis of the Broken Bow uplift as the southern boundary of the sediment volume that might contribute fluids to the Ozark Plateau (with the logic that any sediments south of this divide would expel their fluids south, not north), then the Ouachita-Arkoma sediment volume below 2 km depth is closely approximated by a triangular wedge 12 km deep and 120 km wide (Figure 1C). The volume of such a wedge is 720 km^3 per kilometer strike length. The pertinent strike length of the Arkoma-Black Warrior-Ouachita system that contributed fluids to northern Arkansas and Missouri is ~800 km (see Figure 1) so the total volume contributing fluids to the Ozark area is ~ 566,000 km^3.

The Viburnum Trend deposits contain ~30 x 10^6 tonnes lead (Wiegel, 1965). The Old Lead Belt on the eastern side of the St. Francois Mountains produced about 9 x 10^6 tonnes of lead (Snyder and Gerdemann, 1968). The Tri-State District produced about 14 x 10^6 tonnes of zinc (80%) and lead (20%) (Brockie et al., 1968). The other Central Missouri and Northern Arkansas mining districts contained smaller amounts of metal. All told, the mineralization in Arkansas, Missouri, and immediately adjacent areas totals perhaps ~80 x 10^6 tonnes of combined Pb and Zn.

Basin brines can easily contain ~200 ppm dissolved Pb or Zn (Carpenter et al., 1974). If just 10 ppm lead plus zinc precipitated from basin brines propelled across the Ozarks, 8000 km^3 of brine would be required to precipitate the known resources of the area. This volume of brine represents a brine-filled porosity of less than 1.5% of the 566,000 km^3 of sediments defined above. The sediment volumes identified would have had little difficulty supplying the brine volumes required for mineralization. Quantitative discussion of how basin brines behave as ore fluids has been offered by Sverjensky (1984).

The brines contained in the identified sediment volumes are also sufficient to produce the alteration observed in the Cambrian aquifers of the Ozarks. Gregg (1985) pointed out the extensive nature of the epigenetic dolomite cements at the base of the Bonneterre. He estimated that ~100 km^3 of Bonneterre limestone was dolomitized over a >16,600 km^2 area near the St. Francois Mountains and that 35,000 km^3 of brine would be required by this dolomitization. Even this seemingly very large brine volume represents the brine in pores representing just 6% of the 566,000 km^3 sediment volume. Clearly either cross-basin topographically driven flow or compaction could relatively easily supply the volumes of brine required for alteration and mineralization without exhausting the supply of brine in the Ouachita-Arkoma system.

DISCUSSION, SUMMARY, AND CONCLUSIONS

The calculations presented above are selected to make several specific points. Many different combinations of flow path, focusing, overburden thickness, thermal conductivity, and heat flow could have been selected. The calculations are simple enough using the daisy-chain method that an interested reader can easily explore these possibilities and, I hope, will be encouraged to do so by this discussion.

The calculations indicate the importance of parameters perhaps not emphasized enough in the basin modeling literature. The thermal conductivity of margin cover is critical to the thermal impact of flow. An insulating cover in the Ozarks sufficiently thick to create temperatures similar to those indicated by fluid inclusions in the Cambrian aquifers without fluid flow does not appear to be geologically reasonable, but since the cover has been removed by erosion it is impossible to be completely certain. If the cover insulation was inadequate, the shallow dip of the margin requires rapid flow rates of hundreds of km^3/km/m.y. to elevate aquifer temperatures to the levels indicated by the homogenization data.

In this context, a critical observation is the present distribution of brine in the Cambrian to Mississippian strata in basins surrounding the Ozark plateaus. Across-basin topography-driven flow at 100s of km^3/km/m.y. would flush the brines from the Cambrian and Mississippian aquifers in only a few million years. The fact that brine has not been flushed from these aquifers, but has been flushed by oppositely directed meteoric recharge entering outcrop areas in the Ozark plateaus and is being flushed by cross-basin flow from the Rocky Mountains, requires some explanation. The minimum explanation is that the cross-basin topography-driven flow, if it existed in the Ouachita-Ozark system, was pulsed or episodic.

Several geological arguments suggest that cross-basin hydrologic flow was not operative during mineralization. The very rapid Atokan sedimentation and tectonic thickening of the Permian section during the Ouachita orogeny almost certainly overpressured fluids in the Ouachitas and related basins such as the Arkoma. Overpressuring would have prevented any cross-basin flow during active tectonism and sedimentation. The maximum vitrinite reflectance ($R_o \geq$ 3.0 %) and the highest metamorphic grade occur in the core of the Ouachitas (see Arbentz, 1989). This is not compatible with the cooling by meteoric inflow that would be predicted if cross basin flow were to occur at rates sufficient to warm the Ozark plateaus. Fluid inclusions in Ba-rich adularia dikes and quartz veins in the core of the Ouachita Mountains suggest the outflow of metamorphic fluids at temperatures of up to 300°C (Shelton et al., 1986).

On balance the geological and geochemical evidence seems most compatible with the episodic dewatering hypothesis. Seismic pumping cannot expel sufficient volumes of brine to warm the Cambrian aquifers. Tectonic pulses are of too long duration to be thermally effective. There is no easy way to produce pulsating cross-basin topography-driven flow, since the flow paths have not been sealed by alteration or mineral deposition at their discharge ends. Compaction could easily have expelled a volume of brine sufficient to account for the observed

alteration and mineralization.

One argument used against episodic brine expulsion is that the Mid-Continent deposits do not appear to have been temperature anomalies at the time of ore deposition. The calculations presented in Figure 5 also clearly show that the deposits need not have been local temperature anomalies. Whether or not this is so will depend on how localized the escape from the Cambrian aquifers was and how high (near the paleo-surface) the deposits were in the stratigraphic column at that time. If the deposits were near the Cambrian aquifer source under ~1 km of cover, local thermal anomalies would be lost in the scatter of the homogenization data, and the most obvious signal would be the elevation of temperatures with perhaps some hint of a slight up-dip decrease in the mode of the homogenization data.

Compactive dewatering might have been assisted by a gas drive. The lack of water in the Arkoma (a basin almost literally filled with gas) raises the intriguing possibility that gas generation may have expelled brine, a possibility suggested long ago in general and specifically for the Ouachitas by Rich (1927). Rates of gas-driven brine expulsion are competitive with compaction for moderate kerogen grades and normal sedimentation rates. If the gas generation or gas-driven fluid expulsion occurred in pulses, as particularly organic rich strata were heated or as seals ruptured, for example, the rate of expulsion could have been substantially faster.

Regardless of their cause, pulses of fluid flow are suggested by a variety of observations and have geochemical advantages when it comes to alteration. For example, Sverjensky (1981) documents at least eight pulses of mineralization interspersed with periods of ore dissolution in the Buick mine of the Viburnum trend. Hagni (1976) notes eight intervals of chalcopyrite and pyrite deposition, six intervals of sphalerite deposition, and five intervals of galena and quartz deposition in the Tri-State district of Kansas, Oklahoma, and Missouri. Hagni (1976) comments (p. 487): "The deposition of metallic sulfides took place over a long period of time. This condition is attested to by the many repetitions in the paragenetic sequence... and is suggested by the wide range of Pb isotopes recorded from the center to the edge of a single crystal... The sulfides were even subject to periods of corrosion between periods of deposition...". The corrosion could be produced by meteoric recharge of the Ozark Cambrian aquifers (as is happening today) between pulses of brine expulsion. The low Fe and Mn content of sparry dolomites in the back reef area of the Viburnum Trend suggest this recharge (Buelter and Guillemette, 1988). The pressure-temperature incompatible mineralogy (Barton, 1981) and stable isotopic evolution (reviewed above) also indicate pulses of fluid flow with minerals deposited at different temperatures along perhaps many prograde-retrograde thermal excursions. Pulses of fluid flow can achieve a cumulatively greater alteration because alteration occurs mainly when fluids flow through temperature gradients and the thermal front of an expulsive pulse provides a steeper gradient than the 0.09°C/km average paleogradient across the Ozarks. Pulses of flow could also mature hydrocarbon gases that would react with sulfate to provide the reduced sulfur for base metal sulfide deposition (Anderson, 1991).

Some aspects of the fluid inclusion data just briefly mentioned in the literature may provide critical evidence. Gregg and Shelton (1989a) point out that early fluid-inclusion studies by Roedder and later studies by Bauer found a high-temperature, low-salinity population of fluid inclusions. Fluid inclusions at any given homogenization temperature in fact range from low to high (brine) salinities. The lower salinity inclusions occur in the dolomite cements from late diagenesis through ore deposition time (Shelton et al., 1992).

There are at least three possible explanations for the low salinity inclusions. They could record pulses of metamorphic fluids from the core of the Ouachita Mountains. Fluid inclusions with homogenization temperatures up to 300°C and salinities of 3 wt% NaCl equivalent are found in Ba-rich adularia in organic-rich seams in Cambrian shales on the shores of Lake Ouachita in Arkansas (Shelton et al., 1986). Alternatively they could reflect pulses of cross-basin hydrologic flow. In either of these two cases, pulses of low salinity fluid would flush brine out of flow channels and trap low salinity fluid inclusions. Brines would re-enter the flow channels from less permeable zones after the low salinity and heat pulses had passed. Finally the lower salinity inclusions could be produced by the flow of meteoric water into discharge areas warmed by a pulse of brine outflow. This in fact seems to me the most likely explanation. The 25,000 km study area in southeastern Missouri that Gregg, Shelton, and others have most intensively analyzed, and which now provides the best documentation of the lower salinity inclusions, lies entirely within those parts of the Ozark Plateau where the recharge of meteoric water has displaced brine (dashed box in Figure 4). Thus most if not all of the samples containing lower salinity inclusions could have been affected by meteoric recharge between pulses of brine expulsion. The isotopic composition of the low salinity fluid inclusions and their abundance pattern should distinguish these possibilities.

Observations, modeling, and the possible explanations for the lower salinity fluid inclusions indicate the importance of fluid focusing. Geologic observations suggest some focusing of flow in the Reelfoot rift. Channeling could reconcile steady cross-basin topography-driven flow and the modal fluid inclusion data, but the flow rates would have to be optimum and the lack of salinity flushing would still require flow to be episodic. Channeling in the deeper parts of the aquifers directly affects the combinations of rate of fluid expulsion and overburden thickness that are required to satisfy measured homogenization temperatures in the dolomite in the Ozark plateaus. Definition of the pathways of fluid movement in the discharge areas is necessary for the refined interpretation of fluid inclusion salinity and alteration data.

The above discussion underscores the interrelated regional nature of basin alteration. Low salinity fluid inclusions in Ba-rich adularia in the metamorphic core of the Ouachita Mountains may be related to low salinity, warmer fluid inclusion in the Ozarks, for example. Perhaps we should look past local variations and place alteration in a *far* larger geographic context than has seemed reasonable in the past. The regional fluid flow models discussed here and those that are now appearing in the literature are helpful in encouraging us to do this.

In summary, simple analytical "daisy chain" models show that if the Ozark plateaus' cover was thermally conductive and thin as seems most geologically reasonable, continuous flow at the rates required to explain fluid inclusion homogenization temperatures would have quickly flushed salt from the aquifers in contradiction to present observations. Flow of mineralizing and dolomitizing brines across the plateaus must have been episodic, regardless of the flow mechanism. The most plausible way to produce this kind of flow is episodic compactive expulsion. Meteoric recharge into discharge sites between expulsive pulses is indicated by geochemical zoning in the back reef areas and could explain the low salinity fluid inclusions and the dissolution of sulfides and dolomite.

The analysis depends critically on the following physical factors: (1) the thermal conductivity of Ozark cover, (2) the present day brine distribution in the deeper portions of the Cambrian aquifers surrounding the Ozarks, (3) the focusing of channeling of flow in three dimensions, and (4) the rate of meteoric recharge between pulses of brine discharge. Better definition of the thermal conductivity, pattern of alteration, pattern of pore water salinity, the paragenesis of salinity variations in fluid inclusions, the isotopic composition of the low salinity inclusion fluids, and the regional and local relationships between diverse kinds of alteration and diagenesis in the Mid-Continent could distinguish episodic topographically driven flow from episodic compactive expulsion followed by meteoric recharge. The economic value of base metal cements in the Ouachita-Arkoma Basin-Ozark system has led to unusually good definition of the alteration pattern in this area. Broader and better definition of the pattern could provide particularly clear insights into how fluids move in sedimentary basins, an issue of fundamental concern to both the hydrocarbon and minerals industries.

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