Reactive Flow Models of Ore Formation in the Southeast Missouri District

MARTIN S. APPOLD†, * AND GRANT GARVEN

Department of Earth and Planetary Sciences, Johns Hopkins University, Baltimore, Maryland 21218

Abstract

Two-dimensional numerical reactive transport modeling was used to investigate the deposition of Pb-Zn-Cu ores in the Southeast Missouri district, central United States, by two potential mechanisms: cooling of a fluid carrying metals and reduced sulfur, and mixing of two fluids, one enriched in metals but poor in sulfur, and the other enriched in reduced sulfur but poor in metals. The mechanisms were studied within the context of the topography-driven ground-water flow regime established in the Ozark region by the Late Paleozoic Alleghanian orogeny. The models integrated geology, fluid flow, heat and solute transport, and chemical reaction, generating the most complete depiction yet of potential ore-forming processes in southeast Missouri.

Both mechanisms were found capable of generating important characteristics of the mineralization patterns observed in the field but fell short in other respects. In models of the cooling hypothesis, mineralization was indeed found to be concentrated within the southeast Missouri portion of the Ozark region. This was primarily because of the fact that mineralizing fluid underwent very little temperature change as it traversed the Ozark region until it arrived in southeast Missouri, where its temperature decreased significantly. The important association of mineralization with local basement highs within the Southeast Missouri district was also produced, caused by local increases of fluid velocity over the crests of the basement highs. Smaller scale models, however, revealed much of the mineralization to be concentrated within the basal Lamotte Sandstone rather than the overlying Bonneterre Dolomite, where it is actually concentrated in the field. This model result stemmed directly from the fact that permeability and, therefore, fluid velocities were higher in the Lamotte than in the Bonneterre. A further discrepancy with field observations was the high predicted concentrations of quartz, which exceeded those of galena by over two orders of magnitude.

Models of the mixing hypothesis also led to the regional concentration of mineralization in southeast Missouri, provided vertical dispersivities in the Lamotte Sandstone and Bonneterre Dolomite, the formations that transmitted the two different types of fluids, were low. When dispersivities were high, mineralization was produced more uniformly along the flow path. In further conformity with field observations, ore was concentrated in the Bonneterre Dolomite and particularly around the basement highs, demonstrating the importance of the Lamotte pinch-outs in causing the fluids to mix. The models reproduced well the observed vertical zonation in metals, which was controlled by the relative solubility differences among the primary sulfide ore minerals. However, though mixing was induced by the configuration of the local geology, its intensity was relatively low, leading to ore grades that were considerably less than would be expected from geochemical grounds alone. Because the flow regime is predominantly laminar, the two fluids tended to miscibly displace one another rather than vigorously mix with one another. While still potentially a viable ore-forming mechanism under conditions of high local dispersivity, high dissolved metal and sulfur concentrations, or high fluid velocity, the mixing hypothesis as typically formulated in southeast Missouri is nonetheless much less efficient than previously supposed. Greater efficiency could possibly be generated by reaction of aqueous species with solid phases in the matrix or gas (e.g., H₂S) being generated in the matrix.

Introduction

The Mississippi Valley-type deposits of the Southeast Missouri district constitute one of the great districts of base metal mineralization in the world. Mined almost continuously since the early 1700s, the district represents the largest known concentration of lead in the Earth's crust. In addition, it is an important producer of zinc, copper, and silver (estimated mass ratios of Pb/Zn/Cu/Ag are 6800:880:160:1; Hagni, 1989) and contains subeconomic, though substantial amounts of cobalt and nickel.

Interest in the Southeast Missouri district has been not only for economic reasons. The question naturally arises as to what sorts of geologic processes were operating to create a local enrichment of metals of such magnitude. Steady progress toward answering that question has been made over several decades of research, and a number of key facts about the origins of the deposits have now become clear. One is that the deposits were formed from fluids that very much resemble modern sedimentary brines (Roedder, 1977; Hagni, 1983; Rowan and Leach, 1989; Shelton et al., 1992). Further, paleomagnetic data indicate a Late Pennsylvanian to Early Permian age for the ores (Wu and Beales, 1981; Wisniewiecki et al., 1983; Pan et al., 1990; Symons and Sangster, 1991). A variety of geochemical data also point to a prevailing south-north component in the direction of flow for the mineralizing fluids (Rowan, 1986; Bueltier and Guillemette, 1988; Farr, 1989; Gregg and Shelton, 1989; Viets and Leach, 1990). These observations taken together have led to the widely held hypothesis that the southeast Missouri ores were formed from northward-flowing fluids set in motion by Alleghanian tectonic activity along the Appalachian-Onacita orogenic belt. Subsequent work by Garven et al. (1993) and Appold and Garven (1999) indicates that the most likely driving force for this fluid motion was topographic relief generated during...
Late Paleozoic uplift of the Arkoma basin. Their calculations showed that flow velocities in the Southeast Missouri district and in much of the Ozark region could have reached several meters per year. These velocities were high enough to advect heat from deeper parts of the basin in sufficient quantities to elevate temperatures to the levels necessary to explain the anomalously high temperatures of ore formation in southeast Missouri. Moreover, high fluid velocities could have contributed to high solute fluxes, beneficial to the creation of an enrichment of metals on the large scale present in the district.

It is clear that the southeast Missouri ores are products not only of hydrology but also of geochemistry. Much effort has been directed toward understanding the geochemistry of ore formation, specifically toward the transport of metals and sulfur and the mechanism that caused their precipitation. Many of the fundamental thermodynamic constraints that govern the problem were worked out by Anderson (1973, 1975). One of the important results of this work was to show that Mississippi Valley-type ore metals such as lead and zinc have very low solubilities in the presence of reduced sulfur, except at low pH. From this, three broad classes of possible precipitation mechanisms have emerged. In the first, deposition of the metal-sulfide ore minerals is brought about by mixing of metals and reduced sulfur that had been transported to the ore deposition site in separate fluids. In the second, metals are transported together with oxidized sulfur in the same fluid, and deposition occurs as a result of the sulfur becoming reduced. In the third, metals and reduced sulfur are transported together in the same fluid, but solute concentrations delivered to the site of ore deposition are considerably less than in the first two mechanisms. However, for this third class, ore precipitation could have been caused by several possible factors such as increase in pH, reduction in salinity, or decrease in temperature (Sverjensky, 1981).

The published literature presents conflicting views as to which of these broad classes of precipitation mechanisms was dominant in southeast Missouri. Ore textures and isotopic compositions have been cited by Sverjensky (1981) as evidence for the coexistence of Pb and reduced sulfur in the mineralizing fluid(s). He points out that this texture could easily be explained by a fluid that was saturated with respect to sphalerite and galena that was subject to slight perturbations in temperature or pH, for example, to cause super- or undersaturation, and hence, precipitation or dissolution of these minerals. Further supporting evidence may be the strong covariance in lead and sulfur isotope compositions of galena (Brown, 1967; Sverjensky et al., 1979; Crocetti and Holland, 1989; Goldhaber et al., 1995). Sverjensky (1981) argues that this pattern could be generated most easily if metals and reduced sulfur had been transported together in the same mineralizing fluids.

Anderson (1991) has advocated the transport of metals with sulfur in an oxidized form. Sulfide precipitation in southeast Missouri would then have been brought about by reduction of the oxidized sulfur through reaction with methane or other organic compounds in the brown rock facies of the Bonneterre Formation.

Plumlee et al. (1994) undertook an extensive reaction path modeling study in which they calculated the products of various hypothesized precipitation mechanisms and compared them to geologic and geochemical data from Mississippi Valley-type deposits throughout the Ozark region. They concluded that the ores of the Southeast Missouri district could best be generated by the mixing of a metal-rich, sulfide-poor fluid with another fluid having the converse properties. In a comprehensive lead and sulfur isotope study, Goldhaber et al. (1995) supported the general conclusion that mixing of this type led to the formation of the ores. According to their interpretation, most of the lead had a source in and was transported through the basal Lamotte Sandstone. The fluid transporting this lead then mixed with H2S-rich fluids traveling through overlying strata (Fig. 1).

### Figure 1: Generalized Stratigraphy of the Ozark Region

<table>
<thead>
<tr>
<th>Formation</th>
<th>Depth (ft)</th>
<th>Age</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cambrian</td>
<td>-1000</td>
<td>Ordovician</td>
</tr>
<tr>
<td>St. Francois Confining Unit</td>
<td>1000-2000</td>
<td>Ordovician</td>
</tr>
<tr>
<td>St. Francois Aquifer</td>
<td>2000-3000</td>
<td>Ordovician</td>
</tr>
<tr>
<td>Ozark Confining Unit</td>
<td>3000-4000</td>
<td>Mississippian</td>
</tr>
<tr>
<td>Ozark Aquifer</td>
<td>4000-5000</td>
<td>Mississippian</td>
</tr>
<tr>
<td>Springfield Plateau Aquifer</td>
<td>5000-6000</td>
<td>Mississippian</td>
</tr>
<tr>
<td>Western Interior Plains Confining System</td>
<td>6000-7000</td>
<td>Penn.</td>
</tr>
<tr>
<td>Lamotte Sandstone</td>
<td>7000-8000</td>
<td>Penn.</td>
</tr>
<tr>
<td>Davis Fm.</td>
<td>8000-9000</td>
<td>Penn.</td>
</tr>
<tr>
<td>Bonneterre Dolomite</td>
<td>9000-10000</td>
<td>Penn.</td>
</tr>
<tr>
<td>Derby-Doerun Dolomite</td>
<td>-</td>
<td>Penn.</td>
</tr>
<tr>
<td>Basement</td>
<td>-</td>
<td>Penn.</td>
</tr>
</tbody>
</table>

FIG. 1. Generalized stratigraphy of the Ozark region (from Appold and Garven, 1999). Major hydrostratigraphic units defined on the basis of hydraulic properties are shown on the left side of the column. Individual formations within these units of particular importance to mineralization in southeast Missouri are designated at right.
The present study seeks further insights into the problem of the formation of the ore from reactive transport modeling, focusing in particular on the factors leading to the localization of the ore. Only a few previous attempts, all of a preliminary nature, have been made to apply reactive transport modeling to southeast Missouri or to other Mississippi Valley-type ores. Lichtner and Biino (1992) investigated dolomitization and the subsequent dissolution of dolomite as a mechanism for precipitating ore. They concluded that the pH increase associated with this mechanism could produce a sizeable orebody in 10^5 yr at darcy flow rates of at least 1 m/yr. More recently, Garven (1995) and Garven and Raffensperger (1997) used reactive transport modeling to demonstrate how reaction of a lead-rich brine with earlier formed pyrite in the country rock can lead to the formation of a large lead orebody through sulfide replacement.

Using reactive transport modeling, it is possible to integrate the mutually interdependent contributions of geology, fluid flow, heat and solute transport, and chemical reaction, providing a more complete characterization of the hypothetical ore-forming processes in action and, hence, of their viability, than has been attempted for southeast Missouri before. This paper explores two important potential depositional scenarios for the ores within the topography-driven hydrologic context established by Appold and Garven (1999). First, the response of a metal and reduced sulfur-bearing brine, saturated with respect to the major sulfide minerals of the district, is examined as it undergoes temperature changes along its northward migration from the Arkoma basin to the Southeast Missouri district. Examined next is the movement of two mineralizing fluids, one enriched in metals but depleted in reduced sulfur, the other enriched in reduced sulfur but depleted in metals, and the mixing interactions occurring between them as they are brought into contact with one another during mineralization.

**Geologic Framework**

The geology of the Southeast Missouri district is described in numerous publications, reviewed most recently by Hagni (1995). Additional information about the wider, regional hydrogeology of the Ozark physiographic province, within which the Southeast Missouri district is contained (Fig. 2a), has been published by Imes (1989, 1990a-g) and Imes and Smith (1990). The southeast Missouri ores are grouped into six major subdistricts of Mississippi Valley-type mineralization, all surrounding a central core of Precambrian basement in the St. Francois Mountains (Fig. 2b). Two of these subdistricts, the Viburnum Trend and Old Lead Belt, account for most of the district's roughly 900 million tons (Mt) of ore (Hagni, 1989, 1995; Ohle and Gerdemann, 1989). The elevated central Precambrian core in the St. Francois Mountains, and numerous smaller outlying knobs and ridges like it, remained emergent as islands throughout much of the time that Late Cambrian seas flooded the region. These so-called "basement highs" had a pronounced effect on sedimentation and facies patterns that developed during this time and on the later Mississippi Valley-type mineralization.

The lithologic unit most strongly affected was the Lamotte Sandstone, the oldest sedimentary unit in the region (Fig. 1). The Lamotte pinches out against many of the smaller basement highs as well as the large central core. A very large proportion of the mineralization in southeast Missouri is associated with these pinch-outs, and clearly they are in some way fundamentally related to the genesis of the ore. The Lamotte can reach thicknesses of up to 120 m in the Southeast Missouri district, though thicknesses of less than 100 m are more typical (Thacker and Anderson, 1979). Lithologically, the Lamotte is predominantly a quartz arenite, grading into arkosic conglomerate near the contact with the igneous basement and grading into dolomitic sandstone near the contact with the overlying Bonneterre Dolomite.

The Bonneterre Dolomite is the principal host for the ore, though some degree of mineralization is found in virtually every stratigraphic unit in southeast Missouri. The thickness of the Bonneterre typically ranges from about 50 to 140 m (Thacker and Anderson, 1979). It generally does not pinch out against the basement highs, except for the central core of the St. Francois Mountains. The Bonneterre is primarily limestone in composition. However, surrounding the St. Francois Mountains, it has been extensively dolomitized and virtually all of the mineralization occurs in dolomitic host rock. This replacement dolomitization is clearly preore, though a genetic link with the ore-forming fluids cannot be ruled out. In contrast, sparry dolomite cement spans the paragenesis and some of it postdates mineralization. Textural facies variations have also served to localize ore. A district-wide association of mineralization with the stromatolite reefs that formed in the shallow-marine conditions on the flanks of the central core of St. Francois Mountains is evident in Figure 2b. More locally within the Viburnum Trend, a porous oolitic grainstone and clastic carbonate horizon, locally termed the No. 5 zone, is a particularly favorable host for ore.

Overlying the Bonneterre is an approximately 50-m-thick sequence of alternating dolomite and shale beds comprising the Davis Formation. The Davis is essentially unmineralized except in areas where it is penetrated by faults from the underlying Bonneterre, or where slumping and brecciation have occurred as a result of solution thinning in the Bonneterre. The unmineralized nature of the Davis, along with its shaley character, are geologic manifestations of its low measured permeability (Imes, 1990f) and indicate that the Davis behaved as an aquitard, confining the hydrothermal mineralizing system to the stratigraphically lower Lamotte and Bonneterre (He et al., 1997).

This hydrothermal mineralizing system was a subset of a much larger ground-water flow system that pervaded the entire stratigraphic column up through Pennsylvanian-Permian-age rocks, the time at which the flow system was set into motion by uplift to the south caused by the Alleghanian orogeny. This ground-water system was also areally extensive, encompassing most of the present-day Ozark physiographic province. The regional lithostratigraphy of the Ozarks has been generalized into a simpler hydrostratigraphy that is defined on the basis of permeability (Imes, 1989, 1990a-g; Imes and Smith, 1990). At the base is the St. Francois aquifer which overlies the Precambrian basement and is comprised of the Lamotte Sandstone and Bonneterre Dolomite as described above. Successively overlying the St.
Francois aquifer are the St. Francois confining unit (which contains the previously described Davis Formation), the Ozark aquifer, the Ozark confining unit, the Springfield Plateau aquifer, and Western Interior Plains confining system. The three aquifers all share the characteristic of being comprised of permeable sandstones and carbonates, though they differ greatly in terms of thickness. The Ozark aquifer dominates the hydrology of the region with its high permeability and great thickness of 300 to 1,200 m. The St. Francois aquifer varies mostly from about 100 to 150 m. The highly eroded Springfield Plateau aquifer is generally no thicker than 120 m and is entirely absent from most of the eastern portion of the Ozark province. The confining units derive their low permeabilities from a combination of high shale contents, tightly cemented carbonates, and the absence of fracture networks.

In contrast to other Mississippi Valley-type deposits, the orebodies of the Southeast Missouri district are composed of a wide spectrum of minerals, though five of these—galena, sphalerite, chalcopyrite, marcasite, and pyrite—greatly predominate. A distinct mineral paragenesis is present in the district, in which iron sulfides appear early and are followed by nickel-cobalt, copper, zinc, and lead sulfides, respectively (Hagni, 1986). Additional nickel-cobalt mineralization, mostly in the form of siegenite \((\text{Co},\text{Ni})_3\text{S}_4\), occurs late in the paragenesis with galena.
Copper, zinc, and iron exhibit a strong spatial zonation in the Viburnum Trend (Childers et al., 1995). Typically, in any given orebody, copper concentrations are greatest on the western side and decrease to the east or southeast, as zinc and then iron peak in concentration. Galena coexists with all three metals but is exclusively present in the easternmost parts of the trend. A notable exception to this tendency is at the Magmont-West mine, located about 5 km west of the main body of the Viburnum Trend, where the opposite pattern is observed (Fennel et al., 1995). A common vertical zonation pattern in the Viburnum Trend is for copper mineralization to be concentrated in stratigraphically low positions, followed by zinc in intermediate positions, and iron sulfides in the highest.

Theoretical Approach

The southeast Missouri ores are the products of a complex set of interactions involving the flow of fluid, the transport of heat and solute, and geochemical reactions among dozens of solute species. To develop a full, robust picture of how the ores were formed, each of these processes must be quantified and considered simultaneously. The present section summarizes the theory used to describe their operation. A detailed derivation of the governing equations and their numerical solution can be found in Raffensperger (1993). Solutions for the simulations that follow were generated using the reactive transport program, RST2D (Raffensperger, 1993; Raffensperger and Garven, 1995a, b).

Subsurface fluid flow is calculated by solving a time-invariant conservation of vorticity expression:

\[ \nabla \cdot \left( \frac{1}{K} \frac{1}{\rho \mu_r} \nabla \Psi \right) = -\frac{\partial \rho_r}{\partial x}, \]  

(1)

which is a statement combining an empirical description of flow through a porous medium (Darcy’s law) and the conservation of mass and energy. The variable \( \Psi \) is the stream function, \( K \) is the hydraulic conductivity tensor, \( \rho \) is the density, \( \rho_r \) and \( \mu_r \) are a relative density and viscosity defined with respect to a reference density and viscosity, \( \rho_0 \) and \( \mu_0 \), in the following way:

\[ \rho_r = \frac{\rho - \rho_0}{\rho_0} \]  

(2a)

and

\[ \mu_r = \frac{\mu - \mu_0}{\mu}. \]  

(2b)

\( \mu \) is dynamic viscosity, and \( x \) is the horizontal coordinate. The dependent variable in equation (1) is the stream function, \( \Psi \), which provides a description of the distribution of streamlines in the flow field. Conventionally, streamlines are instantaneous curves that are at every point tangent to the direction of the velocity of flow. In the formulation used here, a slight modification is employed so that the streamlines represent instead curves that are everywhere tangent to the fluid mass flux vector, \( \rho q \) (where \( q \) is the specific discharge or Darcy velocity), providing a more accurate treatment for variable density fluid-flow problems (Evans and Raffensperger, 1992). Solving for the scalar field \( \Psi \) in equation (1) allows the Darcy velocities, \( q_x \) and \( q_z \), to be calculated via the relationships:

\[ \rho q_x = \frac{\partial \Psi}{\partial x} \]  

(4a)

and

\[ \rho q_z = \frac{\partial \Psi}{\partial z}, \]  

(4b)

where \( z \) is the vertical coordinate.

The temperature distribution in the ground-water flow field is calculated by a conservation of thermal energy equation of the form:

\[ \rho^C_i \frac{\partial T}{\partial t} = \nabla \cdot \left( \lambda_{TT} \nabla T \right) - \rho^C_i \hat{C}^L_{T} \mathbf{q} \cdot \nabla T. \]  

(5)

The equation balances the net rate of heat accumulation in a control volume (the term on the left) with net heat transfer by conduction and ground-water advection out of the control volume (the two terms on the right). In this formulation, \( \hat{C}^L \) stands for the volumetric heat capacity per unit mass, \( \lambda \) is the effective thermal conductivity tensor, \( T \) is temperature, \( t \) is time, and the superscripts \( L \) and \( e \) refer to the liquid and effective saturated porous medium, respectively.

The transport of reactive solute by a fluid through a porous medium is governed by the equation:

\[ \frac{\partial M^T_i}{\partial t} = \nabla \cdot \left( D \nabla M^T_{i,aq} \right) - \mathbf{v} \cdot M^T_{i,aq}. \]  

(6)

Here \( M^T_i \) is the total concentration in moles per liter bulk porous medium of a component divided among all geochemical species, present in both the matrix and in the aqueous phase, whereas \( M^T_{i,aq} \) is the total concentration of a component in moles per liter bulk porous medium divided only among aqueous species. \( D \) is the dispersion tensor, and \( \mathbf{v} \) is the average linear velocity. This equation balances the net rate of accumulation of solute mass within a control volume (the term on the left) with the net rates of mass loss by dispersion and by ground-water advection (the two terms on the right). The volume of the bulk porous medium is the combined volume of the medium’s matrix material and the volume of the fluid contained in its pores. The term “component” refers to a member of a set of linearly independent geochemical species out of which all of the aqueous and mineral species considered in the model were built (cf. Table 1). It is important to point out that although no reaction term is shown explicitly in equation (6), the equation nonetheless takes into account the effect of geochemical reaction on solute transport. This is accomplished through the coupling of the \( M^T_{i,aq} \) term to the mass action equation (7) below in the following way. As long as a particular component is involved only in reactions among aqueous species, those reactions will not alter the concentration of that component as represented in equation (6), i.e., the value of \( \partial M^T_i / \partial t \). If the component is transferred between aqueous and mineral species through mineral dissolution or precipitation reactions, then the value...
of $M^T_{i,p}$ will change, altering the net rate of mass accumulation of that component in an arbitrary control volume.

Chemical reaction in the modeling is subject to the assumption of local equilibrium and is described by mass action expressions:

$$ K = \prod_i a_i^{v_i}, $$

where $a_i$ is the activity of the ith species, $v_i$ is the stoichiometric reaction coefficient for the ith species, and $K$ is the thermodynamic equilibrium constant. The kinetics of the reactions were not considered explicitly, meaning in effect that the rates of reactions were assumed to be fast compared to the rate of ground-water flow. The minerals and aqueous species considered in the calculations are listed in Table 1. Values of the equilibrium constant as a function of temperature and pressure for each reaction were calculated using the program SUPCRT (Johnson et al., 1992), where, to reduce data storage requirements, the pressure at any given temperature was assumed to lie on the liquid-vapor curve for water. Thus, the pressure under which geochemical reactions were assumed to take place in the simulations at a particular location did not rigorously coincide with the pressure actually existing at that location, though this differential between assumed and actual pressure was not found to create significant error in the results.

Activities are related to concentrations and mole fractions through the relation $a = \gamma m$, where $\gamma$ is an activity coefficient and $m$ is either concentration or mole fraction. In the calculations that follow, solid phases were always assumed to be pure rather than solid solutions, so their activities were always equal to 1. The activities of aqueous species were calculated using a high ionic strength form of the extended Debye-Hückel equation (Helgeson, 1969):

$$ \log \gamma = -\frac{A_i Z_i^2 \tilde{I}_i^2}{1 + B_i \tilde{I}_i^3} + \gamma_{A_i NaCl} \tilde{I}_i, $$

where $A_i$ and $B_i$ are the Debye-Hückel coefficients, $Z$ is the charge of the species, $\tilde{I}$ is the true ionic strength, $\tilde{\alpha}$ is the ion size parameter, and $\Gamma_{\gamma}$ is a mole fraction to molality conversion term given by,

$$ \Gamma_{\gamma} = -\log(1 + 0.0180153 m^*). $$

where $m^*$ is the sum of molalities of all solute species.

Just as the geochemical reactions are affected by the hydrology (through its control on temperature and the delivery of solute), the hydrology in turn is affected by geochemical reactions (through their alteration of the porosity and permeability of the matrix as a result of mineral precipitation and dissolution). Knowing the concentrations of all of the mineral phases, the porosity can be calculated from,

$$ \phi = 1 - \sum_{m=1}^{\tilde{\omega}_m} \frac{\omega_m M_m}{\rho_m}, $$

where $\phi$ is the porosity, $\omega_m$ and $\rho_m$ are the molecular weight and density of the mineral, respectively, $M_m$ is the concentration of the mineral in moles per liter bulk porous medium, and $\tilde{\omega}_m$ is the total number of mineral phases precipitated. To calculate the permeability as a function of porosity, an empirical relationship proposed by Walsh (1983) was utilized:

$$ \ln \frac{k}{k_i} = 45.7(\phi - \phi_i), $$

where $k$ is the permeability and is related to the hydraulic conductivity by $K = k \rho g / \mu$, where $g$ is the gravitational acceleration. In this case, the subscript $i$ refers to the initial permeability or porosity.

The transport equations were solved using a Galerkin finite element scheme in space and an implicit finite difference scheme in time. Fluid density and viscosity changes as a function of temperature, pressure, and salinity were computed using equations of state from Watson et al. (1980) and Phillips et al. (1983). The chemical equilibrium calculations were
solved using Newton-Raphson iteration with a direct search optimization algorithm to improve the rate of convergence.

Effects of Regional Temperature Variations on Sulfide Precipitation

Hydrogeologic models of the Late Paleozoic ground-water flow regime that was set into motion in the Ozark region by the topography generated during the Alleghanian orogeny consistently predict a sizable south-north temperature decrease across the Southeast Missouri district in the St. Francois aquifer (Garven et al., 1993; Appold and Garven, 1999; cf. Fig. 3). This temperature decrease was found to vary from about 6° to 35°C over the length of the Viburnum Trend, depending on the values selected from within the ranges most likely for the heat flow and hydraulic conductivities of the major aquifers. South of the ore district and, therefore, earlier along the flow path of the mineralizing fluids, the temperature remained relatively constant. Thus, with respect to the surrounding region, southeast Missouri was an area of maximized temperature variation, a conclusion allowed by

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**Fig. 3.** (a) Ground-water flow and temperature field along the profile A-A’ (cf. Fig. 2a) arising from uplift of the Arkoma basin during the waning stages of the Late Paleozoic Alleghanian orogeny, as calculated by Appold and Garven (1999). Vertical exaggeration is 40:1. Solid lines are streamlines, indicating paths of flow. Arrowheads indicate direction of flow. Since any two adjacent streamlines represent equivalent mass fluxes, the streamlines also give an indication of flow rate, in that the more closely spaced streamlines are in a given region, the higher the flow rates. The streamline contour interval is \(6.1 \times 10^4\) kg m\(^{-1}\) m\(^{-1}\) yr\(^{-1}\). Flooded contour lines are isotherms in degrees Celsius. The boldface horizon running from left to right across the length of the plot represents the height of the Precambrian basement, i.e., its contact with the Lamotte Sandstone. The boldface polygon located at about right-center in the plot is the outline of a zoomed-in region shown in Figure 3b and utilized in the basin-scale reactive transport simulations. (b) Zoomed-in region of the flow and temperature fields of Figure 3a, focusing on the flow path of the mineralizing fluids between the Arkoma basin and the Southeast Missouri district. Flooded contours again correspond to temperature in degrees Celsius. Arrows are velocity vectors whose magnitudes correspond to the reference vectors at right.
the fluid inclusion data but not conclusively corroborated by it (Rowan and Leach, 1989; Shelton et al., 1992). Nonetheless, this localized temperature decrease naturally raises the question of the importance of cooling in contributing to the formation of the ores, which is explored in the ensuing calculations.

**Basin-scale simulations**

**Model description:** The reactive solute transport simulations that follow are set in the hydrologic context established by Appold and Garven (1999). Figure 3 is derived from that work and depicts the flow and temperature patterns of a steady-state simulation considered by the authors to be representative of the ground-water system during the time of ore formation. This ground-water system was assumed to be aligned along the south-north transect shown in Figure 2, since the predominant component of fluid flow seems to have been from south to north, based on the evidence cited previously. It should be noted that the presence of east-west mineral zonation in parts of the Viburnum Trend (Childers et al., 1995), the association of mineralization with the edge of the back-reef facies (Fig. 2), and the concentration of ore on the west side of some of the basement highs (Wagner, 1995) suggests the presence of at least some degree of an east-west component to flow. However, the effects of possible east-west deviations from the purely south-north model orientation were not investigated and are probably best addressed by three-dimensional modeling. A ground-water system with a greater east-west component of flow should look similar to the purely south-north model in the two-dimensional frame of reference of the profile. The greatest differences are most likely to arise from the effect of the central basement core of the St. Francois Mountains—the crest of the Ozark dome, which serves to maximize ground-water velocities and to deflect ground water upward in its vicinity, causing an increase in solute flux and a heightened rate of temperature decline. Thus, fluid originating from the southeast would impinge upon the St. Francois Mountains earlier than in the present case and have correspondingly lower temperatures and velocities in the Viburnum Trend. Fluid originating from the southwest would impinge upon the St. Francois Mountains at about the same time as in the present case but impinge upon them more directly, possibly causing an even greater velocity increase and temperature decrease in the Viburnum Trend.

The reactive transport simulations perform calculations that regenerate similar ground-water flow and temperature fields to those shown in Figure 3, while at the same time treating the added complexity of the multicomponent solute transport and geochemical reactions that operate within them. The values of the physical parameters utilized in the simulations are shown in Table 2. Figure 4 shows the model cross sections corresponding to the profile trends shown in Figure 2. Figure 4a is the complete regional profile, the top surface of which represents the inferred Permian paleotopographic surface. Figure 4b is a close-up of a portion of the regional profile in Figure 4a (outlined in bold and shaded), focusing on the flow path from the Arkoma basin to the Southeast Missouri district. The basin-scale reactive transport simulations presented in this section were all carried out over this close-up subdomain. Figure 4c represents a further reduction in scale, focusing solely on the Viburnum Trend, and is based on a cross section constructed by Anderson (1991). The Viburnum Trend-scale simulations discussed later were carried out over this domain.

**Table 2. Physical Model Parameters**

<table>
<thead>
<tr>
<th></th>
<th>Precambrian basement</th>
<th>Lamotte Sandstone</th>
<th>Bonnetteer Formation</th>
<th>St. Francois confining unit</th>
<th>Ozark aquifer</th>
<th>Pennsylvanian-Permian sediments</th>
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</thead>
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<tr>
<td><strong>Horizontal hydraulic conductivity</strong> $K_x$ (m$^2$/s)</td>
<td>0.001</td>
<td>100</td>
<td>20</td>
<td>0.004</td>
<td>50</td>
<td>2</td>
</tr>
<tr>
<td><strong>$K_x/K_z$ (horizontal: vertical ratio)</strong></td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
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<tr>
<td><strong>Porosity (%)</strong></td>
<td>5</td>
<td>25</td>
<td>20</td>
<td>10</td>
<td>20</td>
<td>15</td>
</tr>
<tr>
<td><strong>Longitudinal dynamic dispersivity</strong> $\alpha_L$ (m)</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td><strong>$\alpha_L/\alpha_T$ (longitudinal: transverse ratio)</strong></td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td><strong>Longitudinal thermal dispersivity</strong> $\epsilon_L$ (m)</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td><strong>$\epsilon_L/\epsilon_T$ (longitudinal: transverse ratio)</strong></td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td><strong>Matrix thermal conductivity</strong> (W/m°C)</td>
<td>3.25</td>
<td>3.0</td>
<td>3.0</td>
<td>3.0</td>
<td>3.0</td>
<td>2.0</td>
</tr>
<tr>
<td><strong>Matrix compressibility</strong> (Pa$^{-1}$)</td>
<td>$1 \times 10^{-10}$</td>
<td>$1 \times 10^{-9}$</td>
<td>$1 \times 10^{-9}$</td>
<td>$1 \times 10^{-9}$</td>
<td>$1 \times 10^{-4}$</td>
<td>$1 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

Basal heat flow = 60 mW/m$^2$
All chemical species, aqueous and mineral, were described in terms of a basis, i.e., a linearly independent set of 17 components. The total concentration of each component, $M_T$, was distributed among various aqueous species and solid mineral phases. The sum of the concentrations of a given component present in all of the different aqueous species at a given location is $M^{\text{aq}}_T$, the total aqueous concentration of that component, and was transported via the transient form of equation (6). Once transport had taken place, the fluid was speciated and mineral saturation indices calculated according to the assumption of local equilibrium. Corresponding changes in mineral concentrations in the hydrostratigraphic units due to precipitation or dissolution were then determined.

The geochemistry of a fluid responsible for precipitating Mississippi Valley-type ores by cooling is constrained by several key thermodynamic relationships discussed in detail by Anderson (1973, 1975). Broadly, such a fluid would be expected to be at least moderately acidic, reducing, and relatively dilute in metal and reduced sulfur content. Table 3 gives a fuller geochemical characterization of such a potential ore fluid, describing the fluid compositions that were used in the modeling. As noted earlier, Table 1 lists the thermodynamic components, aqueous species, and solid minerals, respectively, that were employed. The major ion chemistry was defined using data from Viets and Leach (1990) and Plumlee et al. (1994). Viets and Leach (1990) measured the ratios of dissolved Na, Ca, Mg, K, and Cl in fluid inclusions from several Ozark Mississippi Valley-type districts and found evidence for two distinct brine compositions, a local fluid unique to the Viburnum Trend (other southeast Missouri subdistricts were not examined) and a second brine common to all of the Ozark Mississippi Valley-type districts. Plumlee et al. (1994) used this ion ratio data to calculate likely total concentrations of the elements in the original fluids. The present study uses mainly their calculated major ion concentration data for the regional Ozark brine.

The pH, oxidation state, and minor element concentrations are less precisely constrained by empirical data, and Table 3 has several minor variations from the values used in the study by Plumlee et al. (1994). Taking into account the apparent dolomitizing nature of the ore fluid (Gregg, 1985), the model fluid here was assumed to be in equilibrium with respect to dolomite. Saturation with respect to quartz was also assumed. The dolomitizing nature of the fluid, along with dissolved CO$_2$ data from Landis and Hofstra (1991), led to a calculated pH of about 4.4. The fluid oxidation state was defined by equilibrium between acetic acid and aqueous CO$_2$ (Shock, 1988). Incorporating a $10^{-3}$ molar acetic acid concentration and suppressing the formation of methane yielded a reducing log $f_{O_2}$ value of $-57$. To maximize the amount of galena that could potentially be precipitated from the model ore fluid, saturation with respect to galena and equimolar concentrations of Pb and reduced sulfur were assumed. Other important sulfide minerals—sphalerite, pyrite, and bornite—were also assumed to be saturated in the fluid, and aqueous concentrations of Zn, Fe, and Cu were constrained by equilibria involving these minerals. Not all of the fluid in the porous media of the model profile was assumed to be ore forming, as discussed in more detail later. As shown in Table 3, the nonore-forming fluid was identical to the ore-forming fluid in terms of major element composition but was devoid of metals.

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**FIG. 4.** Model profiles. (a) Largest scale profile, used by Appold and Garven (1999) to reconstruct the hydrologic regime created by Alleghanian uplift. Top boundary of profile reflects inferred paleotopographic surface. (b). Close-up region corresponding to area outlined in bold in (a) and used to carry out basin-scale reactive transport simulations. Shaded area on the left side of the profile represents the approximate extent of the Viburnum Trend subdistrict of mineralization in southeast Missouri. (c). Smallest scale profile, constructed by Anderson (1991). Dark shaded regions show locations of major orebodies.

---

**TABLE 1.** Thermodynamic components employed in the model. Major ion chemistry was defined using data from Viets and Leach (1990) and Plumlee et al. (1994). Viets and Leach (1990) measured the ratios of dissolved Na, Ca, Mg, K, and Cl in fluid inclusions from several Ozark Mississippi Valley-type districts and found evidence for two distinct brine compositions, a local fluid unique to the Viburnum Trend (other southeast Missouri subdistricts were not examined) and a second brine common to all of the Ozark Mississippi Valley-type districts. Plumlee et al. (1994) used this ion ratio data to calculate likely total concentrations of the elements in the original fluids. The present study uses mainly their calculated major ion concentration data for the regional Ozark brine.
that most of the cooling in the profile is predicted to occur within the Viburnum Trend (Fig. 3). Isotherms to the south of the trend in the St. Francois aquifer are largely parallel to the direction of flow, except in the deepest portions of the basin, where temperatures are slightly higher. Temperature, therefore, changes very little along most of the flow path until the Viburnum Trend is reached, causing ore to be greatly concentrated there relative to regions farther south.

Closer examination of Figure 5 reveals a secondary level of galena enrichment occurring over the crests of local basement highs, generally near or along the Davis-Bonne Terre interface and the northern end of the Viburnum Trend. The general affinity of sulfide mineralization for basement highs in southeast Missouri is a widely observed phenomenon (Snyder and Gerdemann, 1968; Gerdemann and Myers, 1972; Kisvarsanyi, 1977), with the orebodies commonly lying above pinch-outs of the Lamotte Sandstone against the basement highs, or above the apices of these highs. In a cooling system, the factors with the greatest potential to affect the localization of mineralization are temperature gradient (which affects the solubility of the minerals) and ground-water velocity (which controls the rate at which ore-forming constituents are delivered). As evident from Figure 3, the temperature gradient across the Viburnum Trend is relatively uniform, whereas the ground-water velocities increase markedly over the crests of the basement highs. These velocity increases result because of fluid being focused through a narrower interval of porous medium between the impermeable basement and the low permeability St. Francois confining unit compared to neighboring regions. Similarly, a general regional south-north increase in fluid velocities in the St. Francois aquifer, probably due to thinning of the aquifer between less permeable layers over the crest of the Ozark dome, causes galena mineralization to be more concentrated toward the northern end of the Viburnum Trend in the model. In part, these numerical results may be a consequence of the two-dimensional nature of the grid, which does not account for the lateral movement of fluid around the basement knobs or the Ozark dome and causes the vertical component of flow perhaps to be higher than it otherwise may be. However, the results of the simulation show the primary role that velocity contrasts play in the localization of ore in a cooling system and demonstrate the

Simulation results: The regional-scale modeling was carried out on the portion of the grid displayed in Figure 4b. Fluid flow and heat transport were calculated at steady-state, whereas solute transport was considered to be transient. In the present simulations, too, the length of the St. Francois aquifer south of the Viburnum Trend was considered source rock for the ore-forming constituents. Further, at each time step, fluid passing through the aquifer was reset to be in equilibrium with respect to galena, sphalerite, bornite, and pyrite, thereby making the aquifer a constant source of metals and sulfur. This condition was stipulated in light of the fact that the Viburnum ores represent multiple pore volumes of fluid over the flow path considered and at the metal and sulfur concentrations required, implying that the mineralizing fluids must have had the concentrations of their ore-forming constituents replenished for much of the duration of the formation of the deposits. The fluid composition in the St. Francois aquifer south of the Viburnum Trend is represented by the data under the heading “Ore” in Table 3. Since the St. Francois aquifer is the host for the ore and is generally considered to be the main source for ore-forming constituents (Doe and Delevaux, 1972; Goldhaber et al., 1995), fluid elsewhere in the grid was assigned the composition shown under the heading “Nonore” in Table 3.

Figure 5 shows the concentration (in moles per liter of bulk porous medium) of galena after 100,000 yr. Subtle variations in the spatial patterns of mineralization among the different sulfide minerals are evident at this scale; however, for the most part, galena is representative of the other sulfide minerals (Appold, 1998) and hence is the only one plotted here. The plot shows significant relative enrichment of galena in the region of the grid corresponding to the Viburnum Trend (approximately the northern or leftmost 60 km of the grid). That this should be the case is readily explained by the fact

![Figure 5. Concentration of galena in moles per liter bulk porous medium precipitated after 100,000 yr due to cooling.](image-url)
general principle that ore would be concentrated wherever ground-water velocities are maximized by features such as high permeability facies or thinning of permeable strata between less permeable strata.

Comparison of the model ore grades shown in Figure 5 does not show a close agreement with those observed in the field. Pb ore grades in southeast Missouri average about 5 percent, or about 0.7 moles galena per liter bulk porous medium. After 100,000 yr, maximum model galena concentrations are only about 2.5 × 10⁻⁴ moles per liter bulk porous medium (cf. Fig. 5). This three orders of magnitude discrepancy is caused by at least two factors. Longer simulation times would clearly raise the overall ore grades. Ground-water flowing at a rate of 3 m/yr through a cross sectional area of 100 m × 10 km (the approximate average thickness of the Lamotte Sandstone and width of the mineralized trend, respectively) with the Pb concentration in Table 3 would require at least 3 m.y. to deposit the estimated 2 × 10¹⁰ kg of Pb present in the Viburnum Trend (Ohle and Gerdemann, 1989), assuming all of the Pb in solution were deposited. A longer simulation time than that shown in Figure 5 would, therefore, be needed to deposit all of the lead in the Viburnum Trend. Another factor is the scale of discretization of the grid. Wide nodal spacing causes the metal concentrations to be computed over a large element volume and, therefore, to be deflated in magnitude. Fining the grid discretization would reduce this effect, but would rapidly increase CPU time requirements for each simulation. A more useful comparison of model and field data may be to consider the total tonnages of Pb precipitated over the entire volume of the trend. After 100,000 yr, using the flow rate and cross-sectional data above, presumably only about 7 × 10⁸ kg of Pb would have been deposited. This mass divided by the 100 m × 10 km × 60 km volume of the trend leads to an average ore concentration of about 6 × 10⁻⁵ moles of galena per liter of bulk porous medium, a value that compares favorably with the ranges predicted in the model, and indicates that the model represents the broad ore-forming processes that would be associated with cooling in the system.

Viburnum Trend-scale simulations

Model description: In order to examine in more detail the effects of temperature change on ore formation in southeast Missouri, reactive transport calculations were also carried out on a small-scale grid, corresponding to Figure 4c, encompassing only the length of the Viburnum Trend. As stated previously, this numerical grid was derived from a cross section of the trend constructed by Anderson (1991) that has the added benefit of showing the rough locations of the major orebodies. The model structure employed here was similar to that used for the basin-scale simulations, with the following minor differences. Three hydrostratigraphic units were considered—the Lamotte Sandstone, the Bonneterre Dolomite, and the St. Francois confining unit. The Precambrian basement was considered impermeable and its upper surface defined the bottom boundary of the grid. The results of the simulation shown in Figure 3 were used to define the thermal and hydraulic boundary conditions of the grid so that the Viburnum Trend-scale simulations that follow would be consistent with this regional hydrologic context. Physical model parameters were taken from Table 2. Geochemically, the grid was everywhere assigned an initial composition equivalent to the nonore fluid shown in Table 3. The right boundary of the grid was treated as a constant source of solute. Fluid entering the grid from the portion of the boundary contained within the Lamotte and Bonneterre had the ore composition of Table 3, whereas fluid entering through the portion of the boundary contained within the St. Francois confining unit had the nonore composition. As before, the simulations were carried out at steady-state with regard to fluid flow and heat transport but transiently with regard to solute transport. The simulations were also fully coupled in the sense that matrix porosity and permeability were allowed to change as a result of mineral precipitation and dissolution.

Simulation results: Figure 6 shows the concentrations of galena, sphalerite, pyrite, and bornite predicted after 100,000 yr. The minerals here show the same general affinity for the basement highs seen in the basin-scale simulation in Figure 5 and recorded in the field (Fig. 4c). Again, the reason for the concentration of mineralization there is the local maximizations in fluid velocity occurring over the crests of the basement highs. That is, because the temperature gradient is fairly uniform across the trend, ore formation is concentrated where fluid velocity is the highest. Fluid velocities are higher over the crests of the basement highs because of matrix conservation as the fluid is focused through a narrower interval of porous medium between them and the overlying low-permeability St. Francois confining unit.

Mineralization in the model is not restricted exclusively to the basement highs. What is more, some of the mineralization patterns deviate significantly from those observed in the field (Fig. 4c). Most notable is the fact that ore in southeast Missouri is found predominantly within the Bonneterre Dolomite, whereas in the model, much of it is predicted to occur within the Lamotte. That the model should predict this for a system in which ore deposition is dominated by cooling follows directly from the preceding discussion. The Lamotte Sandstone is considerably more permeable than the Bonneterre (cf. Table 2), so that higher fluid velocities are generally attained in the Lamotte. Therefore, because the temperature gradient is essentially the same in the two formations, mineralization will be favored in the Lamotte compared to the Bonneterre. This outcome could potentially be altered by the existence of high permeability facies within the Bonneterre. That mineralization in southeast Missouri is strongly facies controlled, typically concentrated in permeable lithologies such as oolitic grainstones, breccias, and reef facies, is a well-established fact (e.g., Ohle and Brown, 1954; Gerdemann and Myers, 1972; He et al., 1997). Hence, if permeabilities in these facies were high enough, then the proportion of mineralization present in the Bonneterre versus the Lamotte would probably be higher than calculated here. In general, model mineralization patterns are much more diffuse than observed in the field. No doubt, mineralization patterns would be refined and the disparity between field data and model results reduced if more detailed information on facies distributions were available and could be incorporated in the model.

Figure 7 shows the concentration of quartz precipitated after 100,000 yr. Several locations in the profile have been flagged, with the concentrations of quartz denoted in bold typeface and concentrations of galena denoted in regular
The results highlight a previously recognized problem for cooling as a potential ore-forming mechanism (e.g., Sverjensky and Garven, 1989; Plumlee et al., 1994), in that concentrations of quartz consistently exceed those of galena by over two orders of magnitude, in contrast to field observations where galena dominates over quartz (Hagni, 1986). The high proportion of quartz to galena arises in the model because of the much higher solubility of silica compared to Pb, and because the incoming model ore fluid is saturated with respect to quartz, a likely assumption since the fluid would have been flowing through a largely quartz arenite aquifer. Thus, for cooling to have been an important ore-forming mechanism in southeast Missouri, quartz precipitation would have to have been inhibited in some fashion.

Mixing of Separately Transported Metals and Reduced Sulfur

One of the limitations, already pointed out, of ore-forming mechanisms such as cooling in which both metals and reduced sulfur are transported in the same solution is the relatively low solubility of base metals such as Pb and Zn in the presence of reduced sulfur (Anderson, 1973, 1975). If the sulfur were transported in an oxidized state with the metals and reduced at the site of ore deposition, or if the metals and reduced sulfur were transported in separate fluids that mixed at the site of ore deposition, in principle, orders of magnitude more metals and sulfur could be transported and, hence, much greater rates of deposition and deposit sizes should be attainable. The simulations that follow examine the case in which metals and reduced sulfur are transported in separate fluids and in which ore deposition is caused by mixing of these fluids.

Basin-scale simulations

The basin-scale reactive transport simulations were carried out using the same solution procedures, thermal and hydraulic boundary conditions, and numerical grid as in the previous basin-scale cooling simulations (cf. Fig. 3) with the exception

Fig. 6. Concentrations in moles per liter bulk porous medium of (a) galena, (b) sphalerite, (c) pyrite, and (d) bornite due to cooling after 100,000 yr.

Fig. 7. Concentration of quartz in moles per liter bulk porous medium precipitated after 100,000 yr due to cooling. Four positions in the profile are flagged and show the concentration of quartz (in bold typeface) and of galena (in regular typeface). Note that the concentration of quartz is always more than two orders of magnitude higher than that of galena.
of the dispersivity values, which were variable as described below. The model ore fluid compositions were based on calculations by Plumlee et al. (1994) and are shown in Table 4. Three fluids were considered: (1) a metal-rich, sulfur-poor and (2) a reduced sulfur-rich, metal-poor fluid, both corresponding to the “Viburnum Trend” and “regional” brines, respectively, of Plumlee et al. (1994); and (3) a fluid depleted in both metals and sulfur, otherwise having the same major element composition as the “regional brine” of Table 4. Based on isotopic and geochemical arguments (Doe and Delevaux, 1972; Sverjensky, 1984; Goldhaber et al., 1995), the Lamotte Sandstone has generally been regarded as the source and conduit for metal-bearing fluid in southeast Missouri. That rationale was preserved in the modeling by assigning the metal-rich fluid of Table 4 to the Lamotte Sandstone. Sulfur-rich fluid must then have been restricted to overlying strata such as the upper Bonneterre (Goldhaber et al., 1995). In the model, these fluids were assigned initially only to the southern part of the flow path leading up to the Viburnum Trend, i.e., from the right boundary of the grid to about the 510-km mark (cf. Fig. 4b). All fluid in all hydrostratigraphic units within the geographic area of the Viburnum Trend was initially assigned the metal-sulfur-poor fluid of Table 4. The model was thus intended to simulate what happened as mineralizing fluids from the south invaded rocks within the district initially saturated with nonmineralizing fluids.

Figure 8a shows the concentration of galena after 100,000 yr for a simulation in which longitudinal dispersivity was everywhere equal to 10 m and vertical transverse dispersivity was everywhere equal to 0.01 m. Similar to the regional cooling simulations, the results show mineralization to be strongly concentrated within the geographic area of the Viburnum Trend and to have a high affinity for the local basement highs. Though similar in appearance, the reasons for these patterns of mineralization are different from those in the cooling simulations and here have more to do with the profound sedimentological changes that occur in southeast Missouri. The results demonstrate quantitatively a process that has long been hypothesized as a mechanism for forming the ores. As metal-bearing fluid flowing through the Lamotte Sandstone impinged upon the low-permeability basement highs at the Lamotte pinch-outs, it was deflected upward into the Bonneterre Dolomite, where it interacted with the reduced sulfur-rich fluid present there and quickly became supersaturated with respect to metal-sulfide ore minerals. This mixing hypothesis of separately transported metals and reduced sulfur is, therefore, also able to provide an explanation as to why ore would be regionally concentrated in southeast Missouri. Simply put, the geologic features (i.e., basement highs and pinch-outs in the aquifer units) that promoted mixing were not present elsewhere along the flow path of the mineralizing fluid except in southeast Missouri.

The regional concentration of mineralization in southeast Missouri in the modeling was found to be strongly contingent

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Table 4. Chemical Composition of Ore and Nonore Fluids Used to Test the Effects of Mixing between Separately Transported Metals and Reduced Sulfur on Mississippi Valley-type Ore Formation in Southeast Missouri

<table>
<thead>
<tr>
<th>Aqueous parameter</th>
<th>Value</th>
</tr>
</thead>
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<tr>
<td></td>
<td>Metal-rich</td>
</tr>
<tr>
<td>pH</td>
<td>4.4</td>
</tr>
<tr>
<td>log fO2</td>
<td>-57</td>
</tr>
<tr>
<td>Pressure (b)</td>
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<tr>
<td>Na&lt;sup&gt;+&lt;/sup&gt; (m)</td>
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<tr>
<td>K&lt;sup&gt;+&lt;/sup&gt; (m)</td>
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<tr>
<td>Ca&lt;sup&gt;2+&lt;/sup&gt; (m)</td>
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</tr>
<tr>
<td>Mg&lt;sup&gt;2+&lt;/sup&gt; (m)</td>
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</tr>
<tr>
<td>H&lt;sub&gt;2&lt;/sub&gt;O (ppm)</td>
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</tr>
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<td>Zn&lt;sup&gt;2+&lt;/sup&gt; (ppm)</td>
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</tr>
<tr>
<td>Cu&lt;sup&gt;+&lt;/sup&gt; (ppm)</td>
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</tr>
<tr>
<td>Fe&lt;sup&gt;2+&lt;/sup&gt; (ppm)</td>
<td>28</td>
</tr>
<tr>
<td>Al&lt;sup&gt;3+&lt;/sup&gt; (m)</td>
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</tr>
<tr>
<td>H&lt;sub&gt;2&lt;/sub&gt;S (m)</td>
<td>4.8 × 10&lt;sup&gt;-7&lt;/sup&gt;</td>
</tr>
<tr>
<td>Cl&lt;sup&gt;-&lt;/sup&gt; (m)</td>
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</tr>
<tr>
<td>CO&lt;sub&gt;3&lt;/sub&gt;&lt;sup&gt;2-&lt;/sup&gt; (m)</td>
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</tr>
<tr>
<td>SO&lt;sub&gt;4&lt;/sub&gt;&lt;sup&gt;-2&lt;/sup&gt; (m)</td>
<td>1.0 × 10&lt;sup&gt;-3&lt;/sup&gt;</td>
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<tr>
<td>Saturated minerals</td>
<td>Dolomite</td>
</tr>
<tr>
<td></td>
<td>quartz</td>
</tr>
</tbody>
</table>

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FIG. 8. (a). Concentration of galena after 100,000 yr due to mixing of a metal-rich fluid flowing through the Lamotte Sandstone and a reduced sulfur-rich fluid flowing through the Bonneterre Formation, assuming a vertical dispersivity of 0.01 m. At this dispersivity value, galena is concentrated within the geographic limits of the Viburnum Trend. (b). Vertical dispersivity increased to 0.5 m. Galena mineralization is not concentrated within the Viburnum Trend but is spread out more or less evenly over the length of the flow path.
upon the existence of low vertical transverse dispersivities in the Lamotte and Bonneterre south of the district. The dispersivity is a parameter used in solute transport modeling to describe the tendency of solute to spread during flow due to differences in fluid travel time at the pore scale (Freeze and Cherry, 1979; Fetter, 1993). The value of the dispersivity typically varies as a function of orientation. Dispersivity values are highest in the longitudinal direction, i.e., the direction aligned with the principal direction of flow, and are lower in the transverse directions, i.e., in the two directions perpendicular to the principal direction of flow. Over most groundwater systems, where flow is predominantly horizontal, the lowest dispersivities are generally in the vertical direction. Field measurements of vertical dispersivities show that they can vary over quite a large range, from about 10⁻³ to nearly 1 m (Kelkar et al., 1992). The measurements also do not show a length-scale dependence, as is observed in the longitudinal dispersivity data. The model vertical dispersivity value of 0.01 m for the simulation in Figure 8a, therefore, falls toward the lower end of this range.

Figure 8b shows the effects of raising the vertical dispersivity to 0.5 m. The plot shows the concentration of galena, which is a product of the dispersion process, after only 10,000 yr. At a vertical dispersivity value of 0.5 m, galena can be seen to form in significant quantities along the flow path south of the ore district, in concentrations that are roughly equivalent to those occurring within the ore district. Hence, increasing vertical dispersivity leads to lower relative ore concentration in southeast Missouri and greater mineralization along the flow path, due to greater amounts of mixing between the Lamotte and Bonneterre fluids occurring enroute as a result of higher mechanical dispersion. Therefore, in order for long distance transport of metal-rich and reduced sulfur-rich fluids to have been possible in separate but adjacent aquifers, vertical dispersivities in the aquifers must have been low. If they were high, then one of the ore-forming constituents must have been derived locally within the Southeast Missouri district, or the constituents must have traversed oblique flow paths.

Viburnum Trend-scale simulations

To understand better how fluids of different composition may have interacted locally in southeast Missouri to form ore, reactive transport calculations were carried out over the grid encompassing the approximate length of the Viburnum Trend (Fig. 4c). These simulations, like the previous ones, were carried out within the hydrologic context depicted in Figure 3. Physical and thermal model parameters were, therefore, the same as those used for the simulation in Figure 3 and are listed in Table 2. The only differences were in the longitudinal and transverse dispersivity values, which in the present case were 10 and 0.5 m, respectively. Fluid flow and heat transport were treated as steady state. Solute transport was treated as time dependent. Fluid compositions used were the same as in the basin-scale simulations and are shown in Table 4. The initial conditions were that the Lamotte Sandstone was considered everywhere to be saturated with the metal-rich, sulfur-poor fluid of Table 4, the upper two-thirds of the Bonneterre Formation with the metal-poor, reduced sulfur-rich fluid, and the remainder of the grid with the fluid depleted in both metals and sulfur. A column of constant solute source nodes was assigned to the right boundary of the grid. The composition of the fluid at each source node was identical to that of the initial fluid of the stratigraphic unit in which the source node was contained. Hence the mineralizing system in the Viburnum Trend in the model was continually being replenished with fresh, unmixed ore fluids arriving from the south. The system was thus allowed to evolve, and changes in fluid composition and mineral concentrations were tracked over time.

Figure 9 shows the concentrations of galena, sphalerite, bornite, and pyrite after 10,000 yr. All four minerals show a pronounced affinity for the basement highs, being concentrated near their apices or along their flanks. As stated before, this is because the basement highs create pinch-outs in the Lamotte Sandstone, causing the metal-bearing fluid traveling through the Lamotte to be deflected upward into the overlying reduced sulfur-enriched strata of the Bonneterre, where mixing and sulfide mineral precipitation occur. Comparison of the simulation results in Figure 9 to the field locations of the orebodies in Figure 4c shows good general agreement in the patterns of mineralization. Better agreement could undoubtedly be achieved by taking into account more of the details of the facies and structural heterogeneity of the system and its three-dimensional geometry. As in the cooling genetic scenario, ore formation would be favored in regions where higher fluid velocities are promoted, since the rate of delivery of ore-forming constituents would be higher. Facies heterogeneities and the permeability heterogeneities that would in all likelihood be associated with them, would therefore be expected to cause further refinement in the mineralization patterns predicted.

An attempt at treating some of the facies heterogeneities is shown in Figure 10. Much of the mineralization in the Viburnum Trend occurs in zones of enhanced permeability within the Bonneterre, e.g., breccia zones such as in the Buick mine (Rogers and Davis, 1977) or oolitic grainstone such as in the Brushy Creek mine (Evans, 1977). Zones of enhanced permeability (by a factor of 10 over the remainder of the Bonneterre) were placed in locations coinciding with zones of mineralization shown in Figure 4c. The results shown in Figure 10a for galena after 10,000 yr show a slight refinement in the localization of mineralization over the more homogeneous case. Mineralization in Figure 10a is generally less spread out and shows better agreement with the locations of known orebodies in Figure 4c than the patterns predicted in Figure 9. The reason for the refinement in mineralization patterns is very well illustrated in the stream function plot in Figure 10b. Fluid flow is drawn strongly toward these high permeability lenses so that they become zones of enhanced potential for ore formation. Overall, however, the basement highs clearly play a stronger role than the high permeability lenses and appear to be the primary, first-order control on the localization of mineralization.

Closer examination of Figure 9 reveals a subtle zonation in the distribution of the four sulfide minerals. The copper mineral, bornite, tends to occur in stratigraphically low positions, whereas sphalerite tends to occur in stratigraphically higher positions. Galena and pyrite tend to occupy intermediate to lower intermediate positions, respectively. These calculated
results are consistent with patterns observed in the field in which copper mineralization generally occurs lowest, followed by lead and then zinc (Ohle and Brown, 1954; Grundmann, 1977; Paarlborg and Evans, 1977; Rogers and Davis, 1977; Hagni, 1995). The patterns can be understood in terms of the solubility relationships of the four minerals.

Figure 11 shows the variation in the saturation index (log Q/K, the quotient of the reaction quotient and equilibrium constant) as a function of aqueous H₂S concentration. The figure is based on the metal-rich fluid (Table 4) employed in the present reactive transport simulations and depicts the changes that would occur as reduced sulfur is added to it. The
metal-rich fluid was assumed to be initially at or near equilibrium with respect to galena, pyrite, and bornite. The fluid was assumed to be undersaturated with respect to sphalerite to reflect better the Pb/Zn ratios observed in the district. The initial undersaturation of sphalerite in the fluid explains its high stratigraphic position. Larger amounts of H₂S needed to be added to the fluid to bring sphalerite to significant levels of supersaturation, compared to the other minerals. These larger amounts of H₂S could not be added until the fluid had reached the higher parts of the Bonneterre, where H₂S concentrations were highest. Insight into bornite mineralization patterns can be gained by noting the large slope of its saturation index curve. Bornite, having the steepest slope of the minerals considered, is therefore very sensitive to changes in aqueous reduced sulfur concentration and becomes very rapidly supersaturated as aqueous H₂S concentration is increased. Bornite, therefore, precipitated as soon as the first increases of dissolved H₂S were encountered and was thus concentrated in stratigraphically low positions. A similar but more muted type of behavior would be expected from chalcopyrite, as the slope of its saturation index curve is steeper than that of galena and sphalerite but not as steep as that of bornite. In the modeling here, however, copper mineralization was dominated by bornite because the metal-bearing fluid was assumed to be initially saturated with respect to bornite and, more importantly, because bornite becomes supersaturated much more quickly than chalcopyrite as H₂S concentration is increased. In the field, however, chalcopyrite is the more abundant of the two copper minerals and may, therefore, indicate that the metal-bearing ore fluid was initially closer to saturation with respect to chalcopyrite and undersaturated with respect to bornite.

Figure 12 shows the concentration of galena deposited after 100,000 yr. Three circles are also shown in this figure with corresponding pairs of numerical values. The values in bold typeface represent the maximum concentration of galena found anywhere within the circled region after 100,000 yr (cf. Fig. 9a). Comparison of these values shows there to have been little overall further accumulation of galena over time. After 100,000 yr, nowhere has the concentration of galena exceeded the maximum concentration of galena of 1.5 × 10⁻³ moles per liter bulk porous medium attained in the grid after only 10,000 yr. Over much of the grid galena concentration has stayed about the same and elsewhere it has actually declined. Thus, after 100,000 yr Pb concentrations still remain about two orders of magnitude lower than average Pb grades reported for the district (Ohle and Gerdemann, 1989). This deficiency cannot be explained by a shortage in the availability of ore-forming constituents in the system, as a constant solute source boundary condition was established along the right margin of the grid. The reason for the overall constancy in galena concentration is illustrated in Figures 13 and 14. Figure 13 shows the concentrations of aqueous PbCl₂⁻ and H₂S after 10,000 and 100,000 yr. From this figure it can be seen that as the metal-bearing fluid in the Lamotte encounters the basement highs and is driven up into the Bonneterre, it pushes away or displaces the sulfur-bearing fluid that was formerly in the Bonneterre. The result is that the two different fluids do not interact with one another to as high a degree as might be expected or hoped. Rather, one fluid tends to miscibly displace the other so that the main parts of the two different solute types, metals and reduced sulfur, dissolved in the two different fluids never interact and mix with one another. Secondly, over time, the sulfur-bearing fluid that was initially in the Bonneterre is displaced into higher stratigraphic levels, i.e., into the St. Francois confining unit. Metal-bearing fluid continues to flow underneath in the Lamotte and Bonneterre. Some mixing of metals and reduced sulfur does occur in the St. Francois confining unit, but the low fluid velocities incurred by the low permeability St. Francois confining unit keep mixing rates low and prevent significant accumulations of sulfide minerals from developing there.

These displacement phenomena are further illustrated in Figure 14. The figure shows relative Pb²⁺ and H₂S concentrations, as a fraction of their maximum, initial concentrations...
in the Lamotte and Bonneterre, as a function of distance along a vertical trajectory, C-C' shown in Figure 13 at times of 10^3, 10^4, and 10^5 yr. Relative degrees of galena saturation are indicated by the shaded fields. The plots demonstrate that it is nearly impossible to bring into contact with one another the highest Pb concentrations originally present in the Lamotte, with the highest reduced sulfur concentrations originally present in the Bonneterre. Only the fringes of the Pb and sulfur solute plumes in the Lamotte and Bonneterre fluids are able to interact with one another and react. One result is that maximum galena supersaturation levels are much lower, about 1.5 orders of magnitude lower, than they would be if the full metal and H_2S concentrations of the Lamotte and Bonneterre could be brought together and react. Secondly, over time, the metal-rich fluid of the Lamotte takes over more and more of the Bonneterre, eventually pushing the sulfur-rich fluid into the St. Francois confining unit, so that the main region of galena supersaturation has moved into the St. Francois confining unit. The result is that galena cannot accumulate very quickly in the Bonneterre beyond time periods on the order of 10^3 yr in the simulation and at longer times in some regions it actually begins to redissolve.

These results point out fundamental limitations of a two-fluid mixing model and suggest that the process may not be as efficient an ore-forming mechanism as is often assumed. The physics of mixing in our numerical simulations is modeled primarily through a Fickian dispersion coefficient, whose magnitude is controlled chiefly by the dynamic dispersivity values discussed earlier. Hence, the model results are sensitive to the magnitude of the dispersivity values used. Higher dispersivity values tend to lead to flatter, more diffuse concentration fronts, whereas low dispersivity values tend to lead to sharper concentration fronts. In either case, however, the qualitative results of only the fringes of the two solute plumes interacting with one another, and of one fluid displacing the other, are preserved.

Discussion

Both of the ore depositional models were able to reproduce some key field observations but failed to reproduce others. The cooling model showed that the Late Paleozoic groundwater flow and thermal regime in the Ozark region was very conducive to the formation and localization of metal-sulfide ores in southeast Missouri by cooling. Perhaps the most important contributing factor was the strong temperature gradient predicted to occur in southeast Missouri, caused by upwelling fluid over the crest of the Ozark dome. Coupled with the absence of significant temperature change leading up to the district from the south, conditions were, therefore, favorable for the regional concentration of mineralization in southeast Missouri.

FIG. 13. Comparison of the concentrations in moles per liter of (a) PbCl_2 and (b) H_2S after 10,000 yr and of (c) PbCl_2 and (d) H_2S after 100,000 yr, as part of the simulation shown in Figures 9 and 12. Note the tendency of the metal-bearing fluid to displace the overlying H_2S-rich fluid, particularly evident over the basement highs.
The presence of the temperature gradient was found to be a robust result from the sensitivity analysis conducted by Appold and Garven (1999), and its predicted size falls within the limits allowed within the resolution of the fluid inclusion data (Rowan and Leach, 1989).

The calculations presented here indicate further that the nature of the flow regime was such that fluid velocities were maximized in southeast Missouri relative to other parts of the profile. Higher fluid velocities translate into higher rates of delivery of ore-forming constituents and, hence, faster rates of ore formation. The cooling hypothesis can, therefore, provide an explanation for one of the fundamental questions regarding ore genesis in southeast Missouri, namely, why ore is concentrated in southeast Missouri and not elsewhere on the flow path. The reason is because of the local maximization in fluid velocities and temperature change occurring within the district compared to the rest of the region.

The basin-scale simulations also predicted a strong affinity of the mineralization for the local basement highs, an important and well-known field relationship in southeast Missouri. This affinity was produced by the local acceleration in fluid velocity created as the fluid was forced through the narrower intervals of porous medium over the crests of the basement highs. How much of this phenomenon is a consequence of the two-dimensional structure of the grid is something that needs to be quantified with three-dimensional modeling. At present, however, it appears that the cooling hypothesis is also able to account for one of the important smaller scale characteristics of mineralization in southeast Missouri.

Modeling at the smaller and more detailed Viburnum Trend scale, however, showed some breakdowns in the cooling hypothesis. The affinity of mineralization for the basement highs becomes less pronounced; the predicted patterns of mineralization are in general much more diffuse than suggested by the field data and are significantly concentrated in places such as the Lamotte Sandstone, where no major ore-bodies are found. That mineralization should be concentrated in the Lamotte Sandstone in the model follows from the fact that the Lamotte's permeability is significantly higher than that of the Bonneterre. On the basis of relative fluid velocity, the Lamotte should, therefore, in general be favored as an ore host over the Bonneterre. Secondly, since the temperature gradient predicted in the Viburnum Trend is much more lateral than it is vertical, a strong inducement for ore precipitation should not be created by fluids rising vertically into or through the Bonneterre.

The relatively uniform and strongly lateral nature of the temperature gradient predicted for the Viburnum Trend means that in a cooling ore-forming scenario, the localization of mineralization will be controlled predominantly by velocity contrasts. These velocity contrasts could in turn be generated by permeability contrasts associated with facies variations. The present level of lithologic detail in the model is very general, but it is conceivable that if more information were available and could be incorporated into the model, and if the permeabilities in some of the known ore-hosting facies were high enough, then greater refinement in the mineralization patterns and better agreement with field data would probably result for a cooling ore-forming mechanism operating in southeast Missouri.

Other important questions regarding the viability of cooling as an ore-forming mechanism center on the amount of time available and the problem of quartz precipitation. From the analysis of Appold and Garven (1999), the indications are that the amount of time available for ore formation was relatively short, i.e., on the order of hundreds of thousands of years or less. In constructing the model ore fluid as described above, the most plausible composition based on fluid inclusion and other geochemical data, coupled with the thermal constraints from the flow modeling, indicate that the metal-carrying
capacity of the ore fluid was probably considerably less than what was necessary to deposit the southeast Missouri ores in a few hundred thousand years or less. In the models, quartz was calculated to precipitate in concentrations about two orders of magnitude greater than galena, though in the field in southeast Missouri, quartz is actually quite rare. The kinetics of quartz precipitation and dissolution are slow compared to other minerals (Lasaga et al., 1994; Rimstidt, 1997), but whether they are slow enough under Mississippi Valley-type ore-forming conditions to inhibit the precipitation of quartz to the extent that it would not be deposited in a much greater proportion relative to metal-sulfide minerals is not yet clear.

It is worth pointing out that the quartz problem will not disappear because other ore precipitation mechanisms are invoked. The temperature gradient in southeast Missouri is a relatively fixed feature of the flow system, so quartz will continue to precipitate regardless of what else may be causing the metal sulfides to precipitate. However, this fact is perhaps yet another argument for the relatively fast deposition of the metal sulfides. If these minerals were deposited quickly, then their proportion relative to quartz would remain high and be consistent with the field observations.

The so-called mixing hypothesis, in which metals and reduced sulfur are transported in separate fluids and mix at the site of ore deposition, succeeded in modeling some of the characteristics of mineralization in southeast Missouri but others, somewhat surprisingly, did not model well. As has been recognized since at least the work of Anderson (1973, 1975), the main advantage of this mixing hypothesis over others, such as cooling, where metals and reduced sulfur are transported together, is its ability to convey large concentrations of ore-forming constituents to the site of ore formation. The results here show that it is in fact physically possible to transport the two different types of ore-forming constituents over long distances in separate but adjacent aquifers, without having them interact to a significant degree along the way. This outcome was obtained in the modeling only through the use of low, though still geologically reasonable, vertical dispersivity values. Under these conditions, ore formation by this mixing and transport mechanism was restricted primarily to the geographic locale of the Southeast Missouri district. This was caused by the pronounced sedimentological and structural changes occurring there compared to the rest of the flow path, namely, the basement highs that create pinch-outs in the Lamotte Sandstone and forced metal-bearing fluid to be deflected upward into the reduced sulfur-rich Bonneterre. Such an ore-forming scenario has frequently been promoted in southeast Missouri (e.g., Snyder and Gerdemann, 1968; Beales, 1975; Evans, 1977; Goldhaber et al., 1995) but has here been given its first quantitative physical demonstration. The mixing simulation results were able to account not only for the regional concentration of ore in southeast Missouri but also for its local concentration around basement highs for the same reasons causing its regional concentration. Further, this mixing mechanism was found capable of reproducing basic metal zonation patterns observed in the district.

Despite these successes, the modeling results also revealed the mixing hypothesis as formulated here to have some important limitations. In these simulations, solute was considered to arrive with fluid entering through the southern boundary of the grid and was not generated within the grid—within the hydrostratigraphic units—as was the case in the basin-scale simulations. The working hypothesis, therefore, was that all of the ore-forming constituents were generated external to the district. Mixing between the two types of ore-forming constituents—metals and reduced sulfur—however, was severely curtailed by the fact that the fluids carrying these separate constituents tended to displace one another, rather than to be entrained within one another. Ore was produced at least initially in locations that compared favorably with the field data (cf. Fig. 9), but the process was inefficient because the main parts of the dissolved metals and reduced sulfur could not come into contact with one another and mix. Only the fringes of the solute plumes could interact with one another, which were at concentrations nearly an order of magnitude less than their maximum values in the interior of the plumes. In fact, in the model, ore deposition occurred only during the earliest stages of the simulation. At later times, ore had not only ceased being deposited but over much of the profile was actually beginning to dissolve slightly. This was because the metal-bearing fluid had gradually pushed the sulfur-bearing fluid into higher and higher stratigraphic levels, until finally the interface between the two fluids, where mineralization could occur, had moved into the St. Francois confining unit, where low permeability prevented the rapid build-up of ore. Previously deposited ore in the Bonneterre was now in contact exclusively with the metal-rich fluid, formerly only in the Lamotte, which was near equilibrium, but slightly undersaturated with respect to the sulfide ore minerals, and therefore led to the gradual dissolution of the orebody.

Part of the apparent inefficiency of the mixing hypothesis may be at least in some measure an artifact of the numerical model structure. For example, the upward migration of the interface between the two fluids in the St. Francois confining unit was probably exaggerated by the two-dimensional nature of the grid, which necessitated that all of the fluid flow over the basement high obstructions rather than around them. The maintenance of this interface within the Bonneterre would have allowed sulfide precipitation to continue there and would have led to higher concentrations than currently predicted (Figs. 9 and 12).

Yet the results presented here seem to be making a fundamental statement about the physical operation of the mixing ore-forming process. For low Reynolds number, i.e., laminar flows, there is not a strong impetus for fluids to mix. Streamlines are largely parallel or subparallel (Fig. 10b) so that any two particles of fluid are not likely to cross paths. At the pore scale, this is less true because of the tortuosity of the pore structure. This tortuosity factor is accommodated by the dispersion coefficient but based on the findings here, does not by any means completely counteract the inhibition toward mixing. In fact, for the dispersivity values used in the modeling, which are near the upper end of the allowable range (Gelhar et al., 1992), the degree of mixing was such that the log Q/K saturation index in the Bonneterre never exceeded 1.5 and was about 1.5 log units lower than would have been obtained if a complete degree of mixing had taken place. For the precipitation of galena, for example, this means that fluids effectively behave as if they only had 15 to 20 percent of the Pb and H₂S that they actually do.
This raises again the question of the duration of time available for ore formation. Assuming that mixing could be maintained indefinitely at this level of efficiency, then even an anomalously metal-rich fluid would have had difficulty in depositing all of the Pb from the Viburnum Trend in the hundreds of thousands of years of time probably available, as calculated by Appold and Garven (1999). At the average linear velocities of 10 m/yr or less that their modeling predicts would have been most likely for the flow system, a 100-ppm Pb fluid (behaving as a 15- to 20-ppm Pb fluid) would then have needed on the order of millions of years, rather than hundreds of thousands of years, to deposit all of the Pb in the Viburnum Trend. Based on these model results, for mixing of separately transported metals and reduced sulfur to have been an effective genetic mechanism for the southeast Missouri ores, then one or more of the following conditions must have existed: (1) either very high Pb concentrations of 100s of parts per million or more in the metal-bearing fluid, (2) very high matrix dispersivities in the ore district coupled with relatively low dispersivities along the flow path leading up to it, or (3) very high average linear velocities greater than 10 m/yr. These results have implications for mixing scenarios beyond the case considered here of mixing between separately transported metals and reduced sulfur. Any genetic mechanism that requires the introduction of a chemical constituent from one aqueous fluid to another to bring about ore deposition will encounter the same inefficiency problem. That is, the fluid mechanics of the mixing process make it inherently less efficient as an ore-forming mechanism than the maximum possible from pure geochemical grounds. Mixing scenarios, such as dilution, that do not require the introduction of a new geochemical species to bring about precipitation would not face this problem.

The efficiency of the mixing process could be greatly increased if at least one of the three conditions mentioned above were true, i.e., if the dispersivities, Pb concentrations, or fluid-flow rates had been very high. The efficiency could also be increased if there were some way in which one of the ore-forming constituents could be intrinsically entrained within the fluid from which it is initially absent. This could happen if the constituent were present in the rock matrix through which the fluid flowed. For example, if reduced sulfur were present in the rock matrix as some preexisting sulfide mineral and dissolved by the invading metal-rich brine, or if H$_2$S gas were being generated from source rocks within the Bonnette and dissolved as the metal-rich brine flowed through them, then this fluid displacement problem would be largely circumvented. The problem could be similarly circumvented if metals were transported in a fluid with oxidized sulfur (i.e., sulfate) and reduction of sulfate to sulfide to cause ore precipitation were brought about by reaction with solid phases in the rock matrix or some kind of a gas.

Conclusions

The cooling hypothesis is able to account for some fundamental features of mineralization in southeast Missouri. Mineralization is regionally concentrated in southeast Missouri because of the relatively large change in fluid temperature occurring across the district, compared to elsewhere along the flow path. Within the district, a secondary level of enrichment of mineralization is predicted to be associated with the basement highs, coinciding with a well-known field relationship. This secondary level of enrichment is caused by local increases in fluid velocity as fluid is accelerated through a narrower interval of permeable aquifer medium, sandwiched between the crests of the basement highs and the overlying St. Francois confining unit. In contrast to field observations, enrichment of mineralization was also predicted in the Lamotte Sandstone due to its higher permeability than other stratigraphic units in the region. Published data constraining fluid geochemistry, along with previous modeling results (Appold and Garven, 1999), suggest that the metal-carrying capacity of the mineralizing fluid was probably too low, given the likely fluid-flow rates and duration of time available for ore formation. The results of the modeling also confirmed the problem of the overabundance of quartz precipitation relative to metal-sulfide minerals, expected from equilibrium thermodynamics in a cooling system where the mineralizing fluid is saturated with respect to quartz.

Simulations of the transport of metals and reduced sulfur by separate fluids flowing through the Lamotte Sandstone and Bonneterre Dolomite, respectively, predict that sulfide ore will be regionally concentrated within the Southeast Missouri district because of mixing at pinch-outs of the Lamotte Sandstone against elevated regions of basement. Smaller scale simulations at the Viburnum Trend scale show mineralization to have a strong affinity for the local basement highs and demonstrate these basement highs to be the primary, first-order control on the localization of mineralization. Long distance transport of metals and reduced sulfur in separate but adjacent aquifers is only possible if dispersivities in the aquifers were low, though not unreasonably low. If dispersivities were high, then mixing and mineralization would have occurred along the entire flow path.

Simulations at the Viburnum Trend scale reproduced key vertical metal zonation patterns observed in the district. These zonation patterns are primarily a product of the relative solubilities of the sulfide ore minerals. Surprisingly, the modeling did not substantiate the rapid deposition and high concentrations of ore that typically have been associated with this genetic mechanism. Further analysis revealed this to be because of the laminar nature of the fluid flow and the general tendency of the two different fluids to displace one another, rather than to mix with one another. On physical grounds, mixing is therefore inherently a much less efficient mechanism for depositing Mississippi Valley-type ores than would be anticipated from purely geochemical grounds. The mixing hypothesis is still a viable ore-forming mechanism, provided that dispersivities, dissolved metal concentrations, or fluid velocities are very high. The efficiency of mixing may also be improved if it is brought about by reaction of a fluid with the solid porous medium or perhaps with gas generated within the porous medium.

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