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AUTHIGENIC KAOLINITE AND DICKITE ASSOCIATED WITH METAL SULFIDES—PROBABLE INDICATORS OF A REGIONAL THERMAL EVENT

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Abstract—Authigenic, well-crystallized kaolinite and dickite occur within sulfide mineral deposits (mine-size to hand-specimen size occurrences) of the Mississippi Valley type in Arkansas, Kansas, Missouri, Iowa, Wisconsin, Illinois, and Indiana. Fluid inclusions in these rocks indicate temperatures of formation as high as 140°C. These authigenic kaolin-group minerals are probable geologic indicators of a regional thermal event. Such elevated temperatures are probably the result of heated waters derived from deeply buried sedimentary or tectonic basins, of passage of the region over a hot spot, or of an episode of thinning of the crustal plate in the mid-continent region.

Key Words—Dickite, Kaolinite, Metallic ores, Morphology, Regional thermal event.

INTRODUCTION

Authigenic, well-crystallized kaolinite and dickite have been observed in paragenetic association with sulfide minerals, such as those found in Mississippi Valey type (MVT) ore deposits. The temperatures of formation of such deposits located in the mid-continent United States have been estimated, from homogenization temperatures of fluid inclusions to have been in the range of 100°–140°C (Leach, 1979; Rowan *et al.*, 1984; Hagni, 1983). Other temperatures measured on fluid inclusions in sphalerite grains that occur in small amounts at many locations in the midcontinent region have ranged from 71° to 118°C (Coveney *et al.*, 1987).

From these observations, two geologic implications follow: (1) the presence of secondarily deposited, authigenic kaolin-group minerals as white veins or partings in otherwise gray sedimentary rocks encourages further search for sulfide minerals in deposits of the Mississippi Valley type, and (2) the wide distribution of such kaolin-group minerals may be plausible evidence of a regional, geothermal event.

The purpose of this report is to describe by means of scanning electron microscopy (SEM) occurrences of authigenic kaolin-group minerals associated with sulfide deposits of the Mississippi Valley type and other scattered occurrences in the mid-continental United States and to evaluate their role as indicators of a regional thermal event.

MATERIALS AND OBSERVATIONS

The kaolinite and dickite illustrated by SEMs in this report were collected from mines, quarries, and outcrops in which clay minerals and sulfide occurred on the same hand specimen or were spatially closely associated. The clay specimens micrographed were freshly broken surfaces or loose clay powder, not processed further except that the clay was sputter-coated with a thin film of gold to carry away excess charge from the electron beam. Scale bars on the SEMs represent lengths in micrometers as indicated. The clay minerals were identified by X-ray powder diffraction (diffractograms not reproduced) because the morphologies of dickite and kaolinite are so similar when viewed through a 10 × hand lens in the field or at 1000 ×, in an SEM, that the two cannot be visually differentiated.

Localities from which clay samples (D = dickite; K = kaolinite) were studied are shown in Figure 1, a map modified from Coveney *et al.* (1987). In the Viburnum, southeastern Missouri lead belt, a single hand specimen of ore from the Fletcher mine (collected by Paul Gerdemann) from the Ordovician Bonneterre Formation had dickite on one side (Figure 2) and kaolinite on the other side (Figure 3). Although the hexagonal plates of dickite in Figure 2 are more nearly uniform in size than are those of kaolinite in Figure 3, such a difference is not universal, as is shown by the well-formed hexagonal plates of kaolinite in Figures 7 and 8. The euhedral shape of the kaolin-group minerals, supported by their well-ordered crystallinity as shown in the X-ray powder diffractograms, is used here as evidence of their authigenic origin. The hexagonal plates are unmistakably distinguishable from the familiar vermicular or book-type stacking of kaolinite formed by the weathering of feldspar, or from the mutual-boundary texture in kaolinitic flint clay (both illustrated by Keller, 1985; Figures 8, 10, 12, 14, 21).

Kaolinite from the Oronogo mine in Pennsylvanian shales (Tarr and Keller, 1937), in the Joplin area of the Tri-State District, is shown in Figure 4. This authigenic kaolinite differs markedly in morphology from the laminated clay in the shales. Dickite from the cinnabar district near Amity, Arkansas, location "D" in

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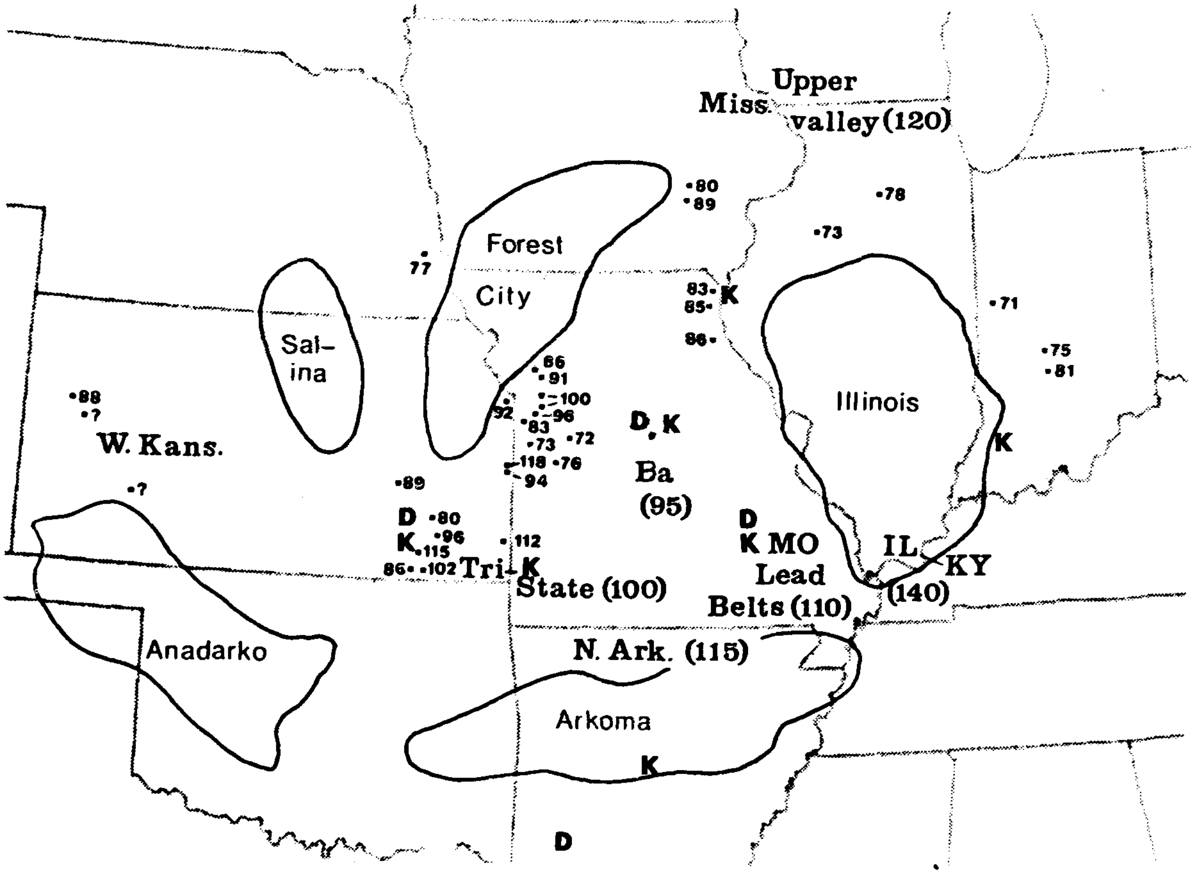
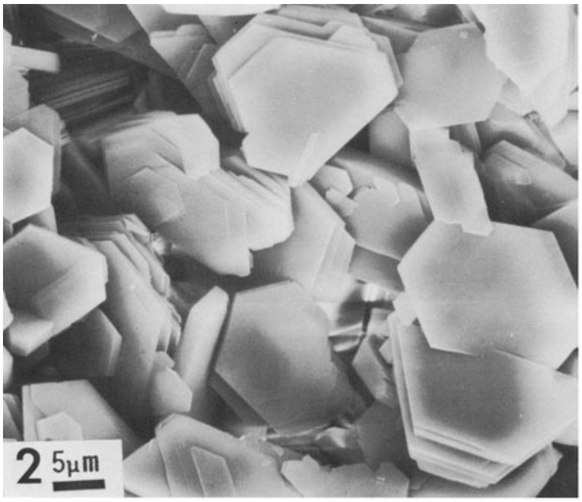
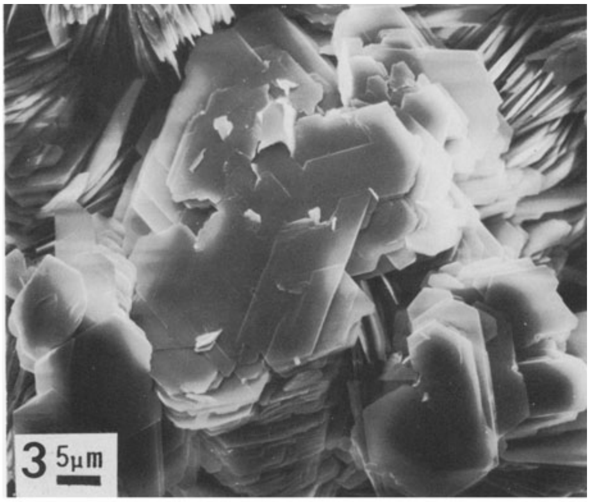


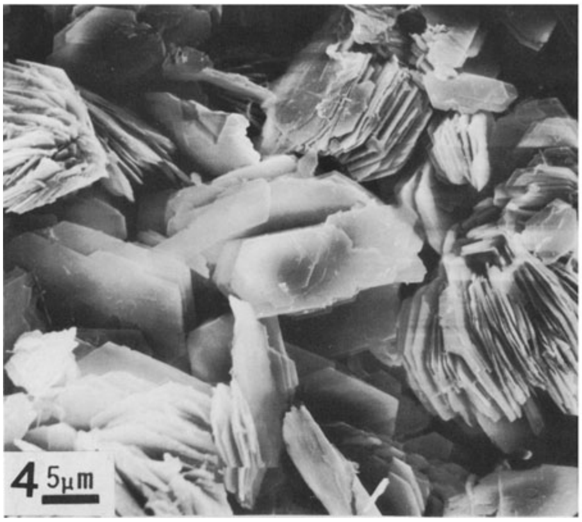
Figure 1. Map after Coveney *et al.* (1987) showing outlines of sedimentary basins in mid-continent United States, locations of authigenic dickite (D) and kaolinite (K), and of sulfide ore districts (characteristic fluid-inclusion temperatures in the district are enclosed in parentheses). Small occurrences of sphalerite in Pennsylvanian-age shales and their fluid-inclusion temperatures determined by Coveney are shown by open numbers and dots. Ore-deposit districts include the Tri-State in Missouri-Kansas-Oklahoma, the southeast Missouri lead belt, the upper Mississippi Valley in Illinois, Iowa, and Wisconsin, the fluorspar district in Illinois-Kentucky, and smaller deposits in Arkansas that are peripheral to the Ouachita Mountain region, an important probable source of mineralizing fluids. The Keokuk occurrence is at the three-corner junction of Iowa, Illinois, and Missouri. The Columbia, Missouri, occurrence is at D, K in the center of the state (Missouri); a small barium deposit (Ba) is located about 75 miles south of this occurrence. The Brazil, Indiana, occurrence of kaolinite, K, is in the southwestern part of Indiana.

west-central Arkansas, is shown in Figure 5 (sample collected by C. G. Stone). Elongate platy crystals, as in Figure 5, are common for the dickite from this mercury deposit. Dickite and kaolinite from Columbia, Missouri (localities D and K in the center of the state), from nearby limestone quarries capped by lower Pennsylvanian chert residuum from the limestone are illustrated in Figures 6 and 7, respectively (Tarr and Keller, 1936). From the quarry where dickite was collected, a tiny crystal of wurtzite, the high-temperature form of ZnS, was found in a vug in the rock. Although crystal morphologies of these two mineral samples are highly similar, the X-ray powder diffractograms clearly differentiate them.

Kaolinite from geodes in the Mississippian Warsaw Shale at Keokuk, southeast Iowa, is shown in Figure 8 (Keller *et al.,* 1966; Hayes, 1967); some geodes contain sparse galena, sphalerite, or millerite. Kaolinite coexisting with sphalerite in the Pennsylvanian Winterset Limestone at Kansas City, Missouri, is shown in Figure 9 (Coveney *et al.,* 1987; specimen furnished by R. M. Coveney). Kaolinite in cracks within siderite concretions in the Pennsylvanian Brazil Formation, Brazil, Indiana (specimen collected by H. H. Murray) is illustrated in Figure 10. In the western part of the mid-continent region, both dickite and kaolinite from the Pennsylvanian Lansing Group in southeastern Kansas were described by Hayes (1967) and Schroeder and Hayes (1968). These authors interpreted the origin of the dickite to be "related in part to igneous activity, but its distribution is regional rather than local." The open numbers on the map of Figure 1 record locations







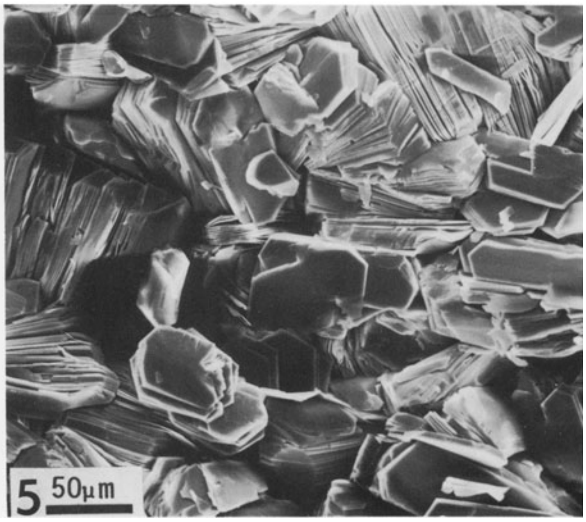


Figure 2. Scanning electron micrograph of dickite in a hand specimen of ore from the Fletcher mine, Viburnum, Missouri. Original magnification = 1800 ×.

Figure 3. Scanning electron micrograph of kaolinite on opposite side of the same hand specimen shown in Figure 2. Original magnification = 1500 ×.

Figure 4. Scanning electron micrograph of kaolinite from the Oronogo mine, Joplin area, Missouri. Original magnification = 2000 ×.

Figure 5. Scanning electron micrograph of dickite from the cinnabar deposit near Amity, Arkansas. Original magnification = 200 ×.

and temperatures measured by Coveney from fluid inclusions in sphalerite.

From isotope studies, the age of the mineralization in the southeastern Missouri lead belt has been found to be between late Pennsylvanian and Permian. The ages of the rocks containing sulfide mineralizations at the other localities described are compatible with the age of mineralization in southeastern Missouri.

By correlating the otherwise independent observations on processes of mineral deposition, elevated temperatures, ages of host rocks, and distribution over a wide region, the following permission inference may be made: namely, that authigenic kaolinite and dickite coexisting with sulfide minerals as found in the Mississippi Valley type deposits are likely indicators of a regional thermal event.

HYPOTHESIZED SOURCES OF ELEVATED TEMPERATURES

Inasmuch as the mid-continent region of the United States may have undergone a regional thermal event, it is intriguing to examine mechanisms that have been proposed for heating that large region. A popular explanation of the simultaneous introduction of ore-

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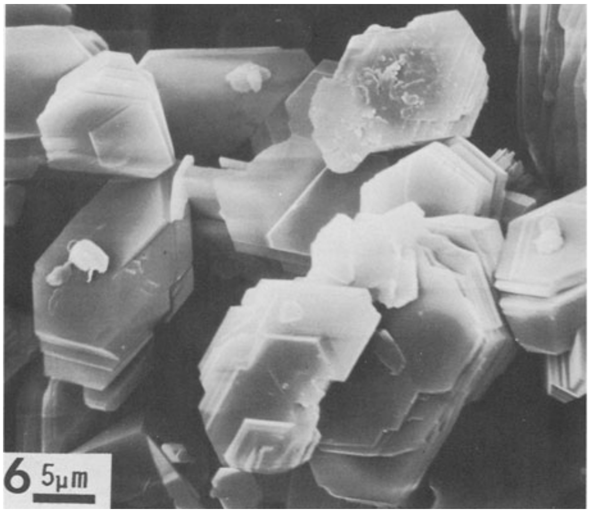


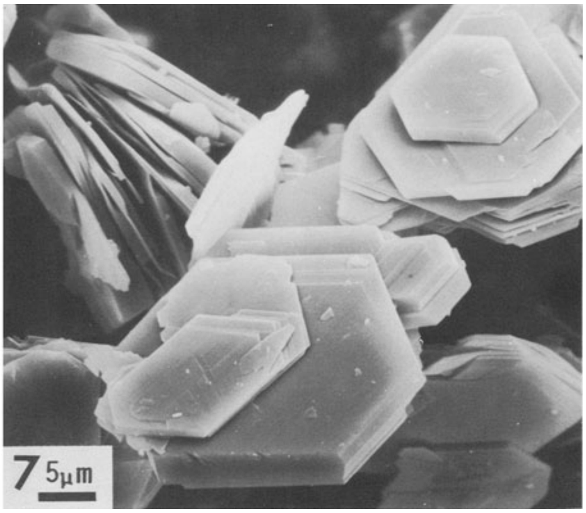
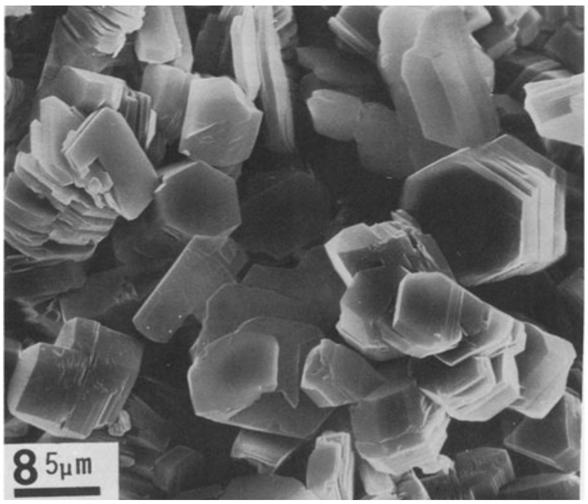


Figure 6. Scanning electron micrograph of dickite from a limestone quarry south of Columbia, Missouri. Original magnification = 2400 ×.

Figure 7. Scanning electron micrograph of kaolinite from a limestone quarry east of Columbia, Missouri. Original magnification = 2000 ×.

forming elements and heating of the rocks is the expulsion of hot water from deeply buried sedimentary rocks in the Ouachita region of Arkansas. Such water has been termed "stratifugic" water (Bethke, 1985). The mode of explusion earliest invoked was ascribed to compaction of the rocks during deep burial (Sharp, 1978). Later studies (Bethke, 1985) inferred that most of the hot water and ore-metal ions were squeezed out of the deeply buried rocks during tectonic compression at the time of the Ouachita orogeny (also dated as late Pennsylvanian or Permian). Most recently, the movement of ground water by gravity flow from deep basins which have been raised and tipped during uplift has been proposed as a means by which heated fluids were carried into shallower sediments (Bethke, 1985). Sites of such basins include at least the Arkoma, Anadarko, Salina, Forest City, Illinois, Michigan, and Upper Mississippi Valley basins, in addition to those shown in Figure 1. Whereas the volumes of such basin-derived fluids appear to be adequate to furnish and transport the dissolved ore-metals for the several Mississippi Valley type deposits, skepticism has been expressed in



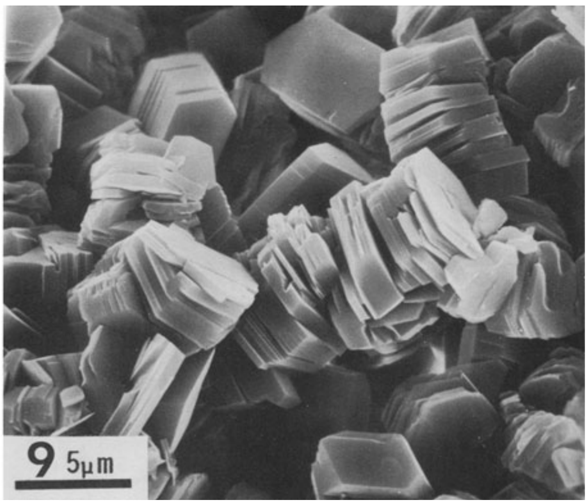


Figure 8. Scanning electron micrograph of kaolinite from a geode at Keokuk, Iowa. Original magnification = 3000 ×.

Figure 9. Scanning electron micrograph of kaolinite, with sphalerite, in the Winterset Limestone, Kansas City, Missouri. Specimen from R. M. Coveney. Original magnification = 4000 ×.

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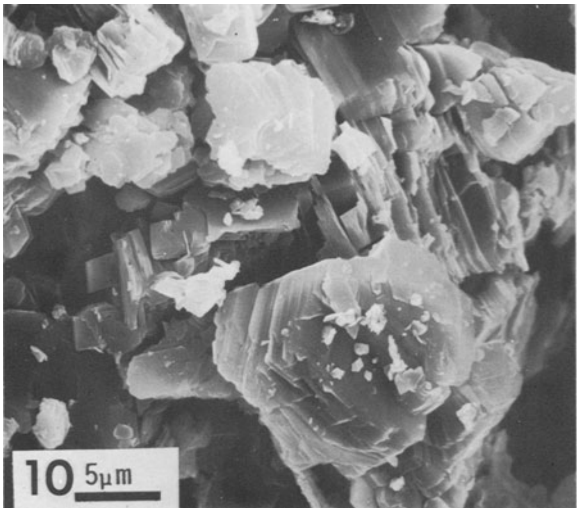

Figure 10. Scanning electron micrograph of kaolinite from a siderite concretion, near Brazil, Indiana. Original magnification = 3000 ×.

informal discussions at meetings as to their adequacy to heat all of the rocks across the wide mid-continent to temperatures measured by Coveney *et al.* (1987).

Alternative processes that might have heated the large area include (1) its passage over a subcrustal "hot spot," and (2) wide-spread stretching and thinning of the earth's crust accompanied by higher heat flow outward. Evidence of volcanic activity in the Paleozoic, but not restricted to late Pennsylvanian to Permian times, is a series of crypto-volcanic explosive events that occurred along the 38th Parallel from the Rose Dome in Kansas to the Hicks Dome in Illinois-Kentucky fluorspar district (Snyder and Gerdemann, 1965; Kisvarsanyi, 1980; Kisvarsanyi and Howe, 1983). Furthermore, the Murfreesboro diamond-producing region, and other peridotite-bearing localities in Arkansas and Kansas, along with numerous peridotitic diatremes in Missouri (Kidwell, 1947; Tarr and Keller, 1933) suggest that this cratonic mid-continent region has been active in vulcanism and tectonism since Devonian time.

Thinning of the crust over such a broad region would have resulted in a wide-spread heat flow that could have raised the temperature of the Paleozoic rock cover, and the water it contained, across all of the mid-continent. Such an episode of stretching of the crust during late Keweenawan to Cambrian time, for example, earlier developed mid-continent rifts and an aulocogen, as was illustrated by Eidel *et al.* (1986). The thinning could have been accompanied also by rise of hot fluids along strike-slip faults that commonly form during crustal stretching. Circulating, heated pore waters in the sedimentary rocks during such an event might have transported sulfide and kaolin-group minerals dissolved from trace disseminations within those rocks and redeposited them within tensionally opened veins and partings. Admittedly, such inference is only permissive speculation, but it merits consideration as the search continues for convincing evidence of the mode of heating the mid-continent region.

CONCLUSIONS

Clay minerals, because of their wide range in geologic occurrence and in crystal morphologies, display in their shapes a vast amount of geologic history, much of which still has not been informatively read from the record in the rocks. In an effort to read the story recorded by authigenic kaolin minerals in wide-spread associations with Mississippi Valley type sulfide minerals, as occur in the mid-continent United States, an interpretation is offered here that this pairing indicates a regional thermal event.

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Note added in proof: A recent article entitled "Supercomputer Analysis of Sedimentary Basins" by C. M. Bethke, W. J. Harrison, Craig Upson, and S. P. Altaner, *Science* **239,** 261–267 (1988) reported numerical experiments on a supercomputer that give insights on how temperatures of 60°–100°C may result from ground-water flow from the Illinois and Arkoma basins, driven by topographic relief on the Pascola arch and Ouchita Mountains. From these brines, ore minerals of Pb, Zn, Ba, and F were precipitated in the Mississippi Valley rocks, clay minerals of the 2:1 layer types were formed during diagenesis, and kaolin was deposited as late cement. Thus, from two clearly different perspectives—field observations of authigenic kaolin polytypes and laboratory supercomputer simulation—similar geologic conclusions were reached.