THE ORIGIN OF MISSOURI FIRE CLAYS

by

W. D. KELLER, JAMES F. WESTCOTT, and A. O. BLEDSOE
University of Missouri, Columbia, Missouri;
A. P. Green Fire Brick Co., Mexico, Missouri;
Bledsoe Mining Co., Belle, Missouri

ABSTRACT

The origin of Missouri fire clays is interpreted from the testimony of the clays in terms of the geologic setting in which they were deposited and developed. Hence, the approach to the interpretation is fundamentally that of sedimentary petrology, rather than economic geology. The clays, as sedimentary rocks, are considered to be the products (mineralogic and geologic) resulting from the responses of their source materials to the energetics of the physical and chemical environments which were impressed upon them during the time interval of their deposition and diagenesis.

The fire clays are inferred to have a sedimentary origin; it is believed that their present-day characteristics were essentially developed in the time intervals of the Cheltenham to pre-Fort Scott (Pennsylvanian) age. The different varieties of fire clay are interpreted as different lithofacies within a continuous Cheltenham deposit. The high-alumina facies (diaspore-burley and boehmite) appears to have been formed by severe leaching on a relatively stable land area, whereas the kaolinitic-illitic facies (semi-plastic to semi-flint clay) seem to characterize products formed near the margin of a slowly sinking depositional region. Both processes of destruction and construction ("katamorphism" and "anamorphism," as used by Van Hise, 1904) appear to have operated in the genesis of the clay minerals.

Evidence points toward a negative Eh and an approximately neutral to slightly acid pH during the formation of the clays. The presence of diaspore and boehmite and the absence of gibbsite in the high-alumina clay are interpreted as indications of leaching of clay minerals under waterlogged conditions. Diaspore may inherit part of the crystal structure and energy of the kaolinite from which it was derived.

INTRODUCTION

The facts that one of the major themes of the program at this Conference on Clays and Clay Minerals is the genesis of clay, and that the conference is held at the University of Missouri make a discussion of the origin of Missouri fire clays very timely. The objectives of this paper are: first, to describe the geologic and mineralogic evidence which bears on the origin of Missouri fire clays, and of the associated rocks of essentially the same age (Pennsylvanian) thought they are barren of economically producible, refractory fire clay; second, to draw genetic inferences from the evidence; and, third, to interpret from those inferences the geological, mineralogical, and chemical environments in which the clay was formed. Finally, a geologic model for the formation of the clay will be proposed. For brevity, only a minimum of stratigraphic detail will be presented; the detailed stratigraphy has been thoroughly covered by McQueen (1943).

Our interpretation of the genesis of the clays departs in many ways, however, from that of McQueen, for much important new evidence bearing on the origin of Missouri fire clay has since become available. This new evidence includes the intact stratigraphic section from the fire clay upward into the Fort Scott limestone in the Bueker pit (Keller, 1952), the numerous identifications of Missouri clay minerals by x-ray and differential thermal analysis, and many data obtained from large numbers of prospect holes drilled across much of the clay-producing areas by power-driven auger, churn, and core drills.

Moreover, we have had the privilege of being able to use the results of countless observations, tests, and other data from work in the field, the laboratory, and the plant of the A. P. Green Fire Brick Company, Mexico, Mo., with which we have been long associated as employees and in other capacities. For these data we wish to give full credit to this company, for it is improbable that any single individual could bring to bear on the topic so many observations or could devote so much time and money solely for research purposes as has the A. P. Green Company.

Contributions and responsibilities by the writers of this report are essentially as follows. Bledsoe has had long familiarity with the district south of the Missouri River and his experience has expedited the field work there; Westcott began differential thermal analysis work on the clays, and has followed with extensive, detailed field and laboratory work on them; Keller has done mineralogic, x-ray, and chemical work on Missouri clays for the past twenty years, coordinated the contributions of the others, and edited this paper.

Missouri fire clays range in refractory quality from semi-plastic, intermediate-duty-fire clay, through high-heat-duty clays and flint clays, to boehmite and diaspore clays. Missouri diaspore runs as high as 79.2 percent Al_2O_3 (theoretically it is 85 percent Al_2O_3, 15 percent H_2O), and its pyrometric cone equivalent, P. C. E., stands not far from that of pure Al_2O_3 which fuses at about 2050°C. The Missouri diaspore deposits are unique, for nowhere else is nearly pure diaspore currently produced in commercial quantity as rock of sedimentary origin. The commercial value of all fire clay and clay products produced in Missouri in 1950 was reported at nearly 38 million dollars (Muilenburg, 1953). Hence, the geologic study of Missouri fire clay deposits comes naturally under the regimen and approach of economic geology. On the other hand, the clays constitute most of the sedimentary rock formation long named the "Cheltenham clay" (new stratigraphic nomenclature may be proposed for this part of the Pennsylvanian in the near future), and therefore inquiry into their origin and geology logically falls equally well within the domain of sedimentary petrology.

From the viewpoint of fundamental petrology, the origin of a rock formation is explained essentially by discovering and interpreting the physical and chemical environments of its source, deposition, and diagenesis, within the geological framework or setting which was present in the particular area during and after the formation of the rock. The chemical environment is to be taken in the broad sense which includes the energetics, the fluids, and the solid states (minerals) of the petrologic system. The final rock (minerals and associated substances comprising it) may be thought of accordingly as the result of the responses of (a) its source materials to (b) the energy impressed upon them within (c) particular chemical and biological surroundings during (d) the time of deposition and diagenesis. The fidelity with which an interpretation can be made of the origin of a rock depends, then, upon the capability and thoroughness with which the observer translates from the effects exhibited by the final rocks the causes which produced them.

To interpret in this paper the origin of the Missouri fire clays, an approach by way of sedimentary petrology will be followed. That the clays are ores is merely incidental, in an economic sense, to their being fundamentally petrologic materials.

I. THE GEOLOGIC SETTING OF THE CHELTENHAM FIRE CLAY

The Geographic Location and Stratigraphic Section

Missouri fire clays in the Cheltenham formation occur across east-central Missouri in a roughly triangular geographic pattern, the southern corner of which is the downfaulted Pennsylvanian blocks near Cook Station and Wesco in Crawford County. The eastern corner is the St. Louis area, and the northwestern corner is in western Audrain or northern Boone County (see Fig. 4). Erosional outliers of fire clay near Versailles in Morgan County and near Aurora in Lawrence County, along with the previously mentioned structural outlier near Cook Station, indicate that fire clay (and Pennsylvanian rocks) were widespread over most of the western flank of the Ozark Dome. The fire clay that remains today has escaped erosion mainly because it was lowered structurally. Flint clay fields north of the Missouri River are located where tributaries to the Missouri have eroded back into and exposed the clay on the south flank of a large shallow syncline which trends northwesterly from St. Louis. Tributaries from the Mississippi River have exposed the fire clay on the north flank of the same structure. South of the Missouri River, only deep pockets of fire clay (mainly flint and diaspore clays) have survived the erosion which took off all overlying Pennsylvanian rocks (except in one small area, the Goerlich Ridge-Bueker pit occurrences, which will be described in detail later); these pockets are widespread over Osage, Gasconade, Maries, Phelps, Crawford, and Franklin Counties.

The Cheltenham fire clays lie above an unconformity which truncates a series of sedimentary rocks (ranging in age from Cambrian to Mississippian), which dip gently in northeasterly, north, and westerly directions from the Ozark Dome. The erosional stage of the unconformity occurred probably shortly after St. Louis (Mississippian) time. A stratigraphic section of the formations encountered most prominently in the clay districts is given below.

STRATIGRAPHIC SECTION

- Post-Pennsylvanian sediments
  - Wind-blown deposits
  - Pleistocene glacial drift
  - Lafayette (?) gravel
- Pennsylvanian System
  - Younger formations of Pennsylvanian age
  - Fort Scott limestone
  - Lagonda formation
  - Bevier formation
  - Ardmore formation
  - Tebo coal
  - Loutre formation
  - Cheltenham clay
  - Graydon formation
- Mississippian System
  - St. Louis limestone
  - *Burlington-Keokuk limestone
  - Sedalia formation
  - Chouteau limestone
- Devonian System
  - Snyder Creek shale
  - (*?)Callaway limestone
- Ordovician System
  - (*?)Kimmswick limestone
  - Plattin limestone
  - Joachim dolomite
  - St. Peter sandstone
  - *Jefferson City dolomite
  - *Roudiboux sandstone and dolomite
- Cambrian System
  - *Gasconade dolomite

The asterisk (*) precedes those formations with which the clay-producing Pennsylvanian is most commonly seen in contact.

The formation immediately above the unconformity is in some places a quartzitic, pyritic, cherty sandstone and elsewhere a sandy, cherty conglomerate-breccia usually referred to as the Graydon formation of the Cherokee Group, Pennsylvanian in age. The sources of the chert and the quartz sand in the Graydon were the abundantly cherty, older Paleozoic limestones, dolomites, and sandstones, which were weathered prior to and during the erosion of the surface of unconformity. During present-day weathering, similar residues of sand and gravel are left behind. Fire clay fills the interstices in the upper part of the Graydon sandstone breccia and continues upward to thicknesses described later.

Fossils are exceedingly scanty in the fire clay but small amounts of coal locally occur in it. A cast of wood (probably *Stigmaria*) by burley diaspore was reported (Keller, 1938) from the Morre diaspore clay pit in Gasconade

County, near Swiss, Missouri. The Pennsylvanian age of beds conformably overlying the Cheltenham is well established by abundant fossils (McQueen, 1943). Hence the evidence is adequate to conclude that following emergence of Mississippian limestones, a long interval of erosion occurred, during which quartz sand and chert gravel accumulated on the weathering land surface in Missouri.

The Physiography of the Lower Cheltenham Surface

In the district north of the Missouri River the fire clay occurs as a blanket deposit, practically continuous, although varying greatly in thick-

PLATE 1. — Panorama across a semi-plastic and semi-flint clay pit near Mexico, Missouri. The sump hole and low spots were filled with fire clay and represent depressions in the pre-Cheltenham topography; the "rises" are old hills rising above the basins. The sump hole contained fire clay to a depth of approximately 60 feet. A thin layer of conglomeratic sandstone lay between the fire clay and the underlying limestone. Photograph furnished by courtesy of the A. P. Green Fire Brick Company.

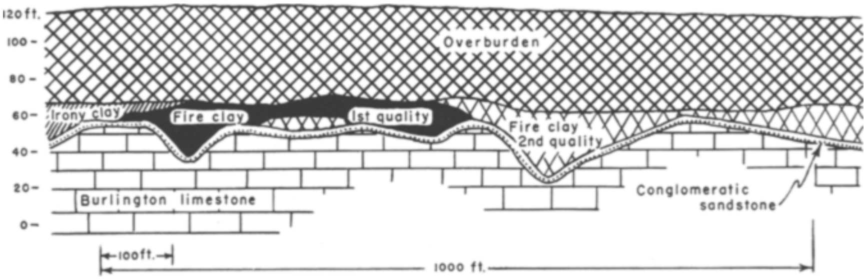

FIGURE 1. — A diagrammatic cross section through a semi-plastic and semi-flint fire clay pit modified slightly (simplified) from actual occurrence. Note that the distribution of quality fire clay in the deposit is independent of stratigraphic control; it is apparently random within one pit and between two or more pits. Source material and local environment were variable during any one time. Cross section after Bradley and Miller.

ness. Its upper surface is essentially a plane, but its lower surface is highly irregular and pockety. In the open pit mines (Pl. 1, Fig. 1) great "rolls" and erosional remnants. Adjacent to them are portions of stream channels, or "horsebacks" of sand- and gravel-mantled limestone rise 10 to 20 feet high, or higher, within the clay deposits. These deposits are thickest (up to about 65 feet) within the irregular basins. The "rolls" are buried hills solution basins and pits, and occasional collapse structures in the limestone beneath.

South of the Missouri River the clay deposits occur predominantly in isolated, individual, elliptical to circular pits which range from a few feet to perhaps 100 yards in diameter and from a few feet to more than 200 feet in depth. Some of the pits are virtual wells; most of them are funnel-shaped with walls converging downward, but others are shallow and basinlike. Geometrically, the receptacles resemble solution basins and sinkholes in limestone (and dolomite), and geologic opinion is regularly in accord with that explanation. That this interpretation of their origin is reasonable is apparent from the present-day occurrence, in the same strata, of caves, large springs, solution channels and basins, and sinkholes, similar in size and shape to those filled with fire clay.

The inference that solution work played a dominant role in the weathering of the limestone-covered land surface across the entire clay-bearing area during post-Mississippian and early Pennsylvanian time is well justified. A karst type of topography is indicated, wherein sinkholes of practically all types were developed: those formed by collapse of the roofs of caverns, by joints being enlarged, and by basins being deepened and widened by solution of the floor and walls concurrent with a variable rate of filling. Mining of clay has exposed certain ill-defined trends of apparently sinuous patterns which suggest that some surface streams connected the Pennsylvanian-age sinkholes.

That this solution-dominated topography was low and marshy, lying probably below the ground-water table, is inferred from the coal deposits associated with the fire clay, from the very fine-grained (colloidal) nature of the clay deposits, and from the vague stream pattern. The presence of muddy, vegetation-laden marshes of this type accords well with the traditional description which is offered in geologic text-books of the environment present during the coal-forming part of the Pennsylvanian.

Of present-day terrains, the Everglade marshes in Florida (before they were drained in part by man) and the cenote region of Yucatan (Urbina, 1910) approach closely the physiographic environment as interpreted for the deposition of the Cheltenham clay. The solution work suffered by the limestones during Cheltenham time appears to have been carried on beneath the ground-water table, according to the process postulated by Davis (1930). The shallower solution basins as manifested by shallower depths of clay pits (usually less than 75 feet), are observed mostly in the semi-plastic clay pits north of the Missouri River. South of the Missouri River, in the flint-and diaspore-clay region, pits are filled with clay to depths ranging in excess of 200 feet.

Although shallow basins of fire clay occur widespread north of the Missouri River, but only predominantly single (less commonly, "twins") isolated deep pits are found south of the river, we emphasize that these single occurrences do not mean that shallow basins did not originally occur south of the Missouri River. We believe that thin, shallow fire clay deposits originally occurred also in the flint and diaspore-clay region in wide-spread patches at or near the top of the Cheltenham, but that almost all of them have been removed by erosion, thereby obliterating the record of their presence. The wide, shallow, irregular, blanketlike occurrences of flint and diaspore clay on Goerlich Ridge (the Bueker pit region) are evidence (Pl. 3) for this conviction. The erosion which removed so much of this blanketlike clay occurred during at least three intervals: first, during Pennsylvanian time, after consolidation of the fire clay but before deposition of an overlying green shale which may be Fort Scott in age (as shown in the Bueker pit); second, prior to deposition of the gravel "hard-pan" of Tertiary (?) age; and, third, during Pleistocene and Recent times.

During most of the early clay-mining period in the flint-diaspore area south of the Missouri River, only single, separated pits were discovered; these numerous observations gave rise to the conclusion that the pits were formed as unconnected, isolated deposits. This conclusion, based on negative evidence, is clearly refuted by the stratigraphic section which was bared later with the opening of the Bueker pit. Here, in the SW¼ NW¼ sec. 30, T. 43 N., R. 5 W., Gasconade County, in a small local, synclinal basin the Pennsylvanian rocks were lowered sufficiently to protect them and their Paleozoic rock cover from erosion. Thin deposits of flint and diaspore clays are found in this locality, spread widely over an undulating floor of shallow, connected basins, but punctuated here and there by a few deeper sinkholes (filled with Pennsylvanian sediments) which extend far below the topmost, connecting clay blanket into the Jefferson City dolomite beneath.

Despite similarity in the depositional basins of the fire-clay districts north and south of the Missouri River, at least two differences distinguish them. South of the Missouri River, the base of solution work was so low that deep (200 feet plus) sinkholes formed; whereas to the north, the base level of erosion was a third to a fourth of that depth. We infer from this, and from other evidence to be stated later, that the southern region was a more positive, higher, and more stable land area than the northern district, and, therefore, that deeper solution basins (sinkholes) formed in the south than toward the north. A second difference is that the clay minerals in the southern (presumably higher land) portion have been leached of silica and fluxing cations to a greater extent than those in the north.

The clay in the deeper pits, as well as that in the shallower basins, is not everywhere of high refractory quality; the geologic mode of occurrence is the same in both types.

In summary, the physiography of central Missouri during Cheltenham time is envisaged as a low-lying, marshy terrain on a limestone and dolomite bedrock which was undergoing erosion by solution. Shallow basins with a depth of about 15 to 20 feet were abundant (a few pockets went deeper, to about 50 feet). South of the Missouri River (upward on the Ozark Dome which was a positive structural element in the Paleozoic) the land rose gradually as the normal surface-drainage gradient of the low-lying region rose with increasing distance from the ocean (which lay toward the north). Deeper sinkholes were formed on this higher land area.

The Sediments Below the Cheltenham

In most places immediately beneath the Cheltenham formation are the quartzitic, pyritic sandstone and the cherty conglomerate-breccia which were assigned earlier to a part of the Graydon formation. The sandstone is persistent and widespread, especially north of the Missouri River, where it overlies the Burlington limestone. It ranges in thickness from a few inches to about 40 or 50 feet in ancient channels, as on Stinson Creek in the south city limits of Fulton. McQueen (1943, p. 34-37) cites several of these occurrences.

South of the Missouri River the sediment corresponding to part of the Graydon may be a conglomerate or a sandstone, but in most places it is a variegated clayey sand or a tripolitic, ferruginous, sandy clay. The variations in lithology, texture, structure, and relationship of this variegated sediment are so wide that they preclude a brief description of them. Probably the rock is best designated as a poorly consolidated, unsorted, nonuniform mixture of quartz silt and sand, chippy tripolitic chert, and variegated clay. The clay is locally unlaminated and slickensided, but elsewhere it is shaly. The variegated colors of this sand-clay-fragmental mixture range widely through white, grays, greens, buffs, red, brown, and purple to almost black. The color patterns may appear speckled, mottled, streaked, and banded, with some boundaries gradational and others sharp. In most places, the pigmenting iron is present in the ferric oxide form, attesting to a positive Eh during deposition or diagenesis. A few dark gray clays in the mixture owe their color probably to carbon, but an oxidized state predominates. The presence of much highly leached tripolitic chert in small chippy fragments supports an interpretation that the source of this variegated, poorly consolidated tripoli-sand-clay mixture was a highly leached, oxidized, surface-weathered residuum derived from the underlying cherty and sandy Paleozoic dolomites and limestones.

Sedimentary structures observed in the mixture are sandstone lenses, contorted strata originating from slump and soft rock deformation, cut and fill, nonpersistent bedding, and beds which sharply thicken and thin. Extreme irregularity in depositional features typifies the formation;

heterogeneity is the only uniform characteristic. The jumbled, contorted, and confused nature of this portion of the Pennsylvanian can hardly be overemphasized. Bretz (1950) took a dozen pages to describe in more specific detail the typical disorganized or chaotic condition of these sediments in several selected exposures which he had examined closely.

Theories previously proposed to account for the origin of this sediment and its striking structures have been well summarized by Bretz, who assigned it to a fill in sink and other types of solution structures. We endorse the assignment of the sediment to a type of fill in solution structures, but emphasize that these mixed sedimentary deposits are not restricted locally to scattered mineral deposits, or to isolated sinkholes and occasional road-cut exposures. The variegated, jumbled clayey sand occurs widespread over essentially all of the clay-producing region south of the Missouri River, and even beyond the fringe areas of economical clay production. Literally hundreds of thousands of prospect holes, drilled by power-driven auger, churn, and core drills at 100 to 300-foot spacings, across thousands of acres of land, have penetrated this variegated, clayey sand, and show its essentially continuous, wide-spread distribution and varying thicknesses as influenced by erratic solution of subjacent limestone.

This variegated, sandy sediment grades in some places upward, through clay rich in iron oxide or quartz, into fire clay; in other places a more or less continuous layer of sandstone may intervene between it and fire clay. The sandstone, when tipped up around a clay pit, locally protrudes in an elliptical to circular resistant outcrop, commonly referred to as the "rim rock". This feature may be a guide to ore (a deposit of fire clay), and was so used in the early days of prospecting for clay when surface indications were sole criteria. That rim rocks are not universally present around clay deposits has been recognized since the search for clay has been extended to drilling for pits that do not show surface indications. Commonly sandstone liners occur within parts of the pits.

Bretz (1950, p. 790) noted that, "Three mechanisms for these subsidence structures have been repeatedly proposed: (1) filling of former topographic sinks, (2) collapse of roofs of former caves, and (3) gradual solution of subjacent calcareous rock with concomitant subsidence of already existing cover rock to become the fill." Bretz emphasized the third proposal, to which the writers add their endorsement and emphasis. All three mechanisms no doubt operated, and many clay pits show evidence of collapse structures with further solution work superimposed; but from the broad geologic viewpoint the mechanism of deepening by a fluctuating rate of solution of subjacent calcareous rocks during deposition was most effective.

To the above-mentioned mechanisms of erosion and fill should be added those of dispersal, transportation, and deposition of clastic sediment by ordinary stream action, for which there is typical and adequate visible evidence in road-cut exposures and natural outcrops. Gross genetic similarity has been noted between certain structures of this Pennsylvanian formation and those of the Shinarump by E. D. McKee (personal communication, 1953) who has studied in detail the Shinarump conglomerate and other ancient stream-channeled deposits of the Colorado plateau.

The surface of unconformity below the Pennsylvanian shows a relief not uncommonly as great as 150 feet; and in some places deep prospect holes have penetrated even deeper (thicker) pits ("wells or chimneys") of sandy clay, ferruginous clay and sand, and poorly consolidated sandstone — these are in addition to the pits of clay which have been mined and expose deep fills. Thus, the pits of clay which are utilized as ore deposits are only one type of filling by detritus in depressions.

Nothing is unique about the physical geologic setting of the clay deposits, and no special case need be made to explain their origin. It is only because this particular kind of filling has been of economic interest to man that it has received attention to the exclusion of the many other deposits of impure clay and worthless sand fill. A sound theory of origin for the fire clay must not ignore its intimate association with numerous non-fire-clay, structurally similar, sedimentary fills.

An interpretation of the geologic conditions that would give rise to the physiographic features described above, and which will account for the origin of basins filled with fire clay, and with other sediments as well, is as follows. Late in Mississippian time, the present clay-producing areas of Missouri were exposed as land. Erosion developed a surface relief of about the same order of magnitude as that which exists there today. The country rock was dolomite (Ordovician) south of the present location of the Missouri River, and limestone (Mississippian) to the north. Erosion of the carbonate rocks was dominated by solution work, and sinkholes, widened joints, and unconnected, or haphazardly connected basins (typical of solution-developed topography) featured the landscape pattern.

Following a period of wide-spread degradation by solution, gentle lowering (perhaps to near sea level) occurred in the clay-bearing district. Aggradation (filling of the solution basins) with detrital material then exceeded removal of limestone by solution. Sandstone and gravel, which remained nearly *in situ* in the northern part of the district, were washed fairly clean of clay (attesting probably to sinking below standing water), and thicker amounts of variegated clayey sand accumulated in the southern part. Stratigraphic evidence of continued sinking in the northern district is given by the northward-thickening wedge of Pennsylvanian sediments which overlies the fire clay, and the flexing of a synclinal structure (visible today) in the same district.

To the south of the present location of the Missouri River, closer to the crest of the Ozark Dome, where overlying Pennsylvanian sediments are thinner, the land must have remained higher and more stable tectonically. Deep sinkholes developed among the shallower basins owing to the height of the land surface. Remnants of these deeper sinkholes hold the diaspore and flint deposits in that district today.

II. THE TESTIMONY OF THE CLAYS AND CORRELATIVE SEDIMENTS

General

The most direct evidence on the origin of Missouri fire clays is in the fire clays themselves. Equally important evidence is taken also from other sediments which are correlative or consanguineous with the fire clay. These sediments include various "impure" fire clays, such as quartz-rich (sand to fine silt), iron-bearing (usually red, purple, or green), and alkali-rich clays, and sandstones and conglomerates which vary widely in clay content. The testimony of these kindred sediments not now classified as fire clay is included because they are important integral parts of the sedimentology of the fire clay, and because some of them without undergoing the least material change may later be reclassified, through the vagaries of economics, into the fire clay category.

Several implications of considerable import suggested above are: first, the origin of Missouri fire clay can not be divorced from the ramifications of a farther-reaching, general sedimentological process without sacrifice of understanding; second, the term "fire clay" is used currently with an economic (dollar value) connotation, rather than with a scientific definition; third, the standards which characterize "fire clay" are quickly changeable and transitory; and fourth, confusion and failure are likely to result if attempt is made to formulate a sound scientific theory of origin of sediments including fire clay which change artificially in category without change in substance.

Numerous examples are well known in the fire clay and fire brick industry where changes in technology, the invention of new machines, utilization of by-products, change in transportation facilities, fluctuation in market demands, or even the enactment of laws which modify the practice or price of labor or transportation may convert "rock" to ore, or ore to waste, and thereby "make or break" a deposit economically. Prior to 1917 a rough-textured waste "rock" was considered an impurity in the flint-clay pits of Missouri, and was discarded by the miners for use as road metal along with the sandstone, dolomite, and low-fusion shale. This "rock" was not included in previous discussions of the origin of the fire clay. After being identified as diaspore in 1917 and after its discovery technologically, the status of this material was changed from "rock" to "clay" and quickly became the most costly and the most sought-for clay in the district. Furthermore, clays which are marginal in "purity" (economic sense) are always subject to rapid and abrupt change from "rock" to fire clay, or vice versa.

We recognize in Missouri fire clays that there is no sharp break in the petrological sequence between Pennsylvanian sandstones of high quartz content and radically different diaspore of high alumina content. Gradual transition can be traced between them, through clayey (also shaly) sandstone, plastic, semi-plastic, semi-flint, flint, and burley clays into diaspore. Likewise, gradual transitions can be traced between fire clays of varying "purity," ceramic properties, and mineral compositions. We do not minimize scientifically the transitional nature of the clays for the sake of a deceptive economic convenience in classifying them artificially and arbitrarily as "sand," "shale," or "diaspore." Instead we regard the continuous gradations in the fire clay and its correlative suite of sediments as normal sedimentary litho-facies changes, and consider that the several, clearly distinguishable, lithologic types present are indicators of the environments in which they were formed.

Geographically, diaspore and boehmite clays (the highest alumina "end members") occur in the southern part of the fire clay area. Semi-plastic and semi-flint fire clay (which are kaolinitic and illitic, and therefore, higher in silica and lower in alumina) occur predominantly in the northern part of the Cheltenham. Flint clay (mainly kaolinitic) is concentrated between the end-member localities, although it occurs in great abundance with the diaspore and also with the semi-plastic clay. Hence, the Cheltenham formation, when viewed broadly as a sedimentary rock formation, shows a litho-facies gradation from high-alumina clay and minerals in the south, to a kaolinitic-illitic suite of minerals and rocks in the northern part of the fire clay district. Further northward from the Ozark Dome the fire clay disappears, and all of the argillaceous rock is shaly, presumably illitic. The whole lithofacies gradation apparently is an expression of variation in the environments of deposition and diagenesis. The causes for the variation will be discussed later.

The Semi-Plastic and Semi-Flint Clays

The semi-plastic and semi-flint Cheltenham fire clays, as typified by the deposits which are mined in the open pits in Audrain, Callaway, and Montgomery counties, occur in essentially a blanket-type deposit which ranges in thickness from almost nothing to about 65 feet. The range in thickness is due to the irregular lower surface, developed unconformably by solution and erosion of the underlying limestone, as has already been described. The upper surface is essentially flat. A 20-foot average thickness provides profitable mining at this time (1953).

During the mining operation, these clays are usually separated into two grades: (1) a lower, harder, more flint-like, commonly dark gray and slightly more refractory clay, occurring in the depressions, and (2) an upper, softer, lighter-colored more plastic, less refractory clay, which is commonly more highly slickensided and slakes more readily in water. In some pits the separation of the clays can easily be made on external appearance, but in other pits laboratory testing is necessary to differentiate them.

In a few pits, clay of only one type (geologic and ceramic) is found. In other pits, three clay variants which differ in recognizable physical appearance, and in parallel ceramic properties, occur as lower, middle, and upper members. These members ordinarily contact each other with irregular large interpenetrations and gradational boundaries. Separation (or grading) of the clays is usually set up on a basis of practical ceramic considerations which are economically significant at the time of mining. These considerations change as ceramic technology evolves, or as the market demand for different types of refractories rises or falls. Hence the division of the Cheltenham fire clay by the clay producer into more than two members is usually governed by artificial, economic, or technologic reasons rather than by genetic differences. For these reasons, it usually is unsound geologically to describe a stratigraphic section from the fire clay produced in one pit and impose it in geologic detail on the clay in neighboring pits or on the Cheltenham formation in general. McQueen (1943) appears to have been led astray in this respect.

Fire clays vary significantly in ceramic properties from pit to pit much as coal lenses occur, disappear, or vary widely within the coal-producing portions of the Pennsylvanian. For example, a coal lens occurs above the fire clay at the pit of the Mexico Refractories Company which supplied over 2,000 tons of good bituminous coal. A half mile distant it disappears, or occurs as a thin, dark film in the section. Hence, the classic "layer-cake" geologic concept of constant, uniform, and wide-spread sedimentary beds does not apply in this part of the geologic column where many local variations in marshes, lagoons, hills, and streams were apparently present during sedimentary deposition.

Mineral and chemical compositions. — Mineralogically, the fire clay in the lower part of the pits is composed of a mixture of kaolinite (more or less disordered) and usually some illite, perhaps up to 20 per cent. More or less quartz in the size range from clay to fine sand may accompany the clay minerals. The presence of a considerable proportion of quartz in the clay removes it from the fire-clay category because the quartz brings the clay-quartz system down in the direction and vicinity of the eutectic point in the Al_2O_3-SiO_2 system, and thereby lowers the fusion temperature of the clay to an intolerable degree.

X-ray powder diffractograms of the clay show sharp and intense basal reflections, but those from pyramidal and some prismatic planes are diffuse or lacking. Hence, disorder is indicated in the stacking within the fire clay crystals, but orderliness appears to increase as the clay becomes "harder" and approaches flint clay. The latter gives an x-ray pattern, Figure 2, closely similar to one of well-crystallized kaolinite. The basal spacing of the semi-flint and semi-plastic fire clays is of the order of 7.2 to 7.3 A, which suggests the presence of some interlayer water. Differential thermograms run on sensitive apparatus[1] show water loss between 100° and 200°C; older less sensitive apparatus did not detect significant amounts

---

[1] Courtesy of R. S. Green, Breckenridge laboratory of the A. P. Green Fire Brick Company.

of water (Keller and Westcott, 1948). Both hydrated kaolinite and illite would lose water at low temperature. The gross mineralogy which we have outlined is simple and adequate, we hope, to contribute to the broad geologic picture. At for the detailed mineralogy of these clays, most of the work is still to be done.

At least two different major types of plastic to semi-plastic fire clay are within close (geographic) occurrence. Variation in both the stacking(?) within the kaolinite, and the amount of illite (and chlorite ?) present, probably are important factors causing the differences. Detailed mineralogic studies of the clay will probably provide explanations for certain physical and ceramic properties not now understood. A study correlating the types of plastic clays with their distribution in the semi-plastic region is under way. A chemical analysis of typical lower Cheltenham semi-flint clay is given in no. 3 of Table 1.

TABLE 1. CHEMICAL ANALYSES OF MISSOURI FIRE CLAYS

No.	1	2	3	4	5
SiO_2	3.89	44.42	45.92	48.90	56.10
Al_2O_3	76.21	38.63	35.79	33.20	24.47
Fe_2O_3	0.98	0.55	0.75	1.47	3.64
TiO_2	3.52	2.12	2.28	1.58	1.58
CaO	0.08	0.04	0.06	0.56	0.61
MgO	0.06	0.10	0.36	0.34	1.11
Na_2O	0.79	0.30	0.44	0.10	0.17
K_2O	0.24	0.12	0.41	1.53	2.89
H_2O	14.56	13.90	13.06	11.55	8.39
Total	100.33	100.18	99.07	99.29	99.27

1. Diaspore clay, NE¼ SE¼, Sec. 29, T. 41 N., R. 7 W., Maries County, Mo. (McQueen, 1943, p. 163)
2. Flint fire clay, SE¼, Sec. 19, T. 51 N., R. 1 W., Lincoln County, Mo. (McQueen, 1943, p. 47)
3. Semi-flint fire clay, NW¼, Sec. 29, T. 47 N., R. 3 W., Warren County, Mo. (McQueen, 1943, p. 50)
4. Semi-plastic fire clay, A. P. Green Fire Brick Co., Pit No. 4, Audrain County, Mo. (McQueen, 1943, p. 58)
5. Plastic "foundry" clay, A. P. Green Fire Brick Co., Pit No. 4, Audrain County, Mo. (McQueen, 1943, p. 64)

The clay in the upper part of the Cheltenham (if and where an upper part is differentiable from the lower) is also chiefly kaolinite, but it commonly carries more illite, especially in the finer colloidal fraction, than does the lower part. Usually the P.C.E.[1] of the upper clay shows less refractoriness; this is a probably negative correlation with increasing illite (potassium and other fluxing metal cations) content. A typical

---

[1] Pyrometric cone equivalent (P.C.E.), is a measure of the fusion temperature of a substance under an arbitrary, standard rate and environment of heating.

chemical analysis of this clay is given in no. 4 of Table 1. Of genetic significance is the fact that the upper part of the clay shows less effect of leaching (*i.e.*, less removal of alkali, alkaline earth, and other metallic cations which lower the fusion temperature of clay) than does the lower part. Hence, to propose that leaching by downward-moving water removed soluble cation fluxes and raised the refractoriness of the clay, as has been done elsewhere, is in conflict with the observable facts that the upper part of the clay, which would be leached most intensely by the freshest water moving downward, has actually been leached the least. Some other mechanism, perhaps upward leaching during dialysis, can better explain the process of refining the Cheltenham fire clay.

Imperfect crystallization of the kaolinitic mineral referred to is interpreted as evidence against a severe or intense degree of downward surface leaching of the parent material. Severe leaching, by either supergene or rising low-temperature hydrothermal waters, traditionally implements well-crystallized kaolinite, but this is not characteristic of Missouri semi-plastic fire clay.

Texture of the fire clay and its genetic implications. — The texture of the semi-plastic and semi-flint fire clays is commonly that of random (criss-cross) orientation of clay-mineral crystal aggregates. It contrasts with the laminated texture of shales, which is due largely to the stacking of clay-mineral flakes one upon the other in parallel to subparallel arrangement (See photomicrographs, Pl. 2). The criss-cross orientation of fire clay mineral crystals is interpreted as arising from the haphazard and random growth of crystal aggregates of clay minerals crystallizing within a quiet, fairly homogeneous body of mud or gel that is essentially physically isotropic. The clay plates in a laminated marine shale, on the other hand, are initiated as a result of the flocculation of clay as it enters saline water, after which flakes grow as it settles through or is washed about in the water containing a high concentration of effective cations (Keller, 1946; Ingram, 1953).

The growth of clay-mineral crystal aggregates in the fire clay may have been constructive, *i.e.*, growth from less well organized (structurally) hydrated silica, hydrated alumina, and/or hydrated alumino and aluminum silicates which originated as products of weathering from a distant source. On the other hand, clay-mineral formation may have been destructive, *i.e.*, by the removal (essentially *in situ*) of cations of silicates that were rich in alkalis, alkaline earths, and other metals (in other words, "weathering of primary silicates"), and by the further degradation of prior clay minerals.

It is not impossible that both of the above mechanisms operated side by side in the movement of alumina and silica toward a state of equilibrium as is represented primarily by the kaolinite-type mineral (an intermediate material between the other extremes of ions in solution and partly leached solids). Under this interpretation, the mud gels probably were comprised

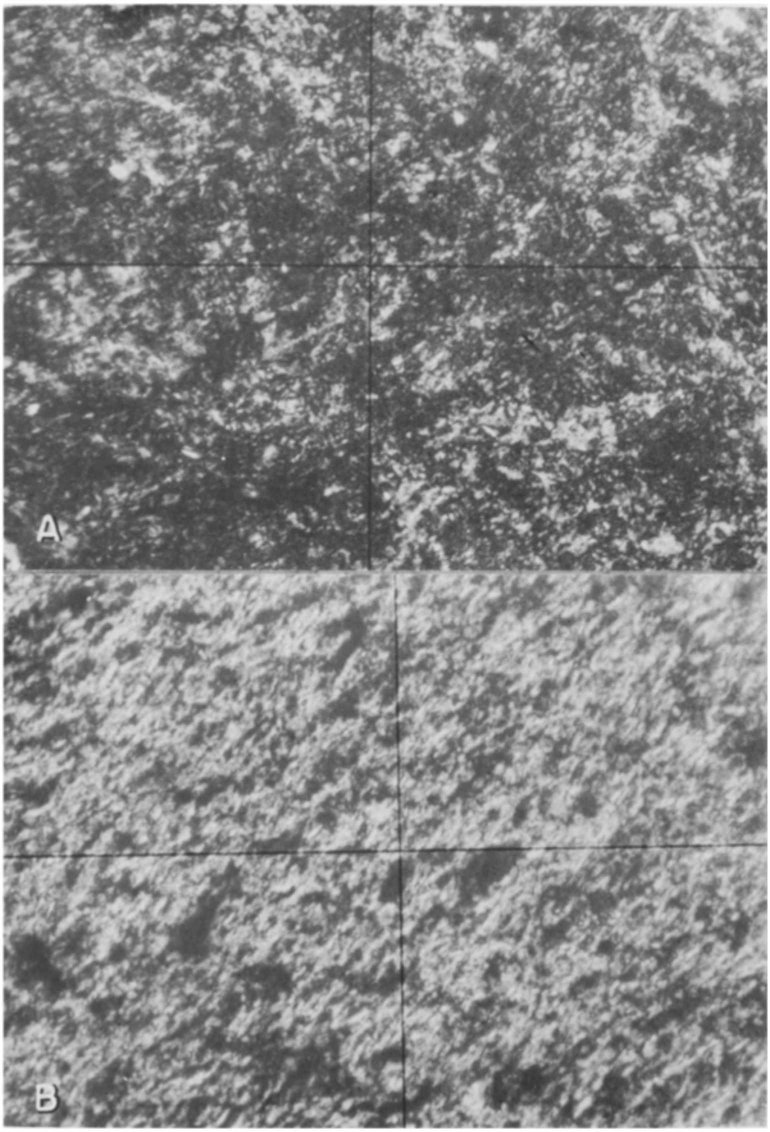

PLATE 2. — Photomicrographs of thin sections: (A) Cheltenham semi-flint fire clay. Shows the random, criss-cross orientation of clay crystals in non-laminated fire clay. Interpreted that the clay crystals formed in a relatively homogeneous clay gel. Crossed Nicols, original magnification, 150 x. (B) Lagonda shale which occurs not far above the Cheltenham. Note the parallelism of clay flakes which is reflected megascopically in the lamination and fissility of the shale. Crossed Nicols, original magnification, 450 x.

of colloidal-size clay-mineral crystals and hydrated alumina and silica, mixed with organic matter which was also largely colloidal.

Marshes and swamps in which the Cheltenham fire-clay mud accumulated are envisaged as being similar to parts of the present-day Everglades. The latter are in depressions similar to the postulated Cheltenham basins even to the extent of having originated by the erosion and solution of underlying limestone. Florida basins are low-lying with respect to sea level, and in some the water alternates between fresh, brackish, and marine types. This alternation is brought about by slight changes in elevation, the blowing in of ocean salt, a rise or fall of the ground-water interface between fresh and marine water, or by increased influx of fresh water from excess precipitation or flooding.

Changes in environment such as indicated above should be reflected by changes in the composition, (and possibly in the texture) of the clay minerals occurring and forming within them. In this way, a significant difference in the clay mineralogy of neighboring or adjacent deposits might be produced, and if the salinity varied during the filling of one basin, the clay mineralogy of the deposit might vary vertically in a corresponding manner. The physical setting postulated above (and exemplified in part by the Everglades marshes) accounts logically for the wide variation in properties of Cheltenham deposits which occur adjacent to each other.

Organic residues and pyrite which are in the Cheltenham clay (most commercial refractory fire clay is selected free of pyrite) point toward a negative Eh in the deposit during and after deposition. The presence of considerable (10 to 40 percent) illite intermixed with kaolinite suggests that the hydrogen ion concentration was not high (probably not acid), and that potassium ions were abundantly available. A modern marine environment is hospitable toward illite formation. A mixture of illite with dominant kaolinite suggests, therefore, that the water in which the Cheltenham semi-plastic clay was formed was probably fresh to partly brackish, and not far from neutrality in pH.

It is inferred, therefore, that the semi-plastic to semi-flint facies of the Cheltenham fire clay was deposited in a low-lying marshy terrain which had been developed on limestone bedrock at the beginning of Cheltenham time in a region near the ocean. This land surface on the limestone was irregular, with low to moderate relief, as shown by the prominences and basins in the floors of the clay pits. The presence of enclosed (undrained by surface streams) depressions in the limestone attests to their origin by solution work, and slump structures (found infrequently) in the clay and limestone are evidence of cavern collapse. Hence, solution work was prominent in the limestone prior to the time of clay deposition. Solution of the limestone continued prominently throughout the time of deposition of the clay, as may be inferred from the slickensides in the clay, from the slump features, and from the differential sag structures shown in clay-coal and in light-dark clay strata. Because of the low elevation of the land

and of probable heavy rainfall (evidenced by the coal-producing, luxuriant vegetation in Pennsylvanian time), the soil and underlying rocks would have been water-logged, and water would have stood relatively high in the marshes.

Clay was washed into the marshes along with silt and fine sand. While the coarser clastics remained in the channels of moving water, clay colloids probably passed through a filterlike screen of plants growing around the quieter pools, thereby concentrating fire clay substance in the protected basins. The sources of the clay were the Jefferson City dolomite in the south and the Burlington limestone in the north. The clay mineral fraction (less than two microns in effective settling diameter) isolated from the Jefferson City dolomite showed in x-ray pattern that "illite is represented, and a diffuse band is well developed where the kaolinite line (basal spacing) would occur. The DTA is not clearly diagnostic but the presence of kaolinite is suggested" (Robbins and Keller, 1952, p. 149). In the Burlington limestone pattern, "montmorillonite, illite (?), and weak kaolinite and quartz lines are present in the x-ray diffraction pattern. The DTA accords with that determination" (Robbins and Keller, 1952, p. 149). Hence, some kaolinite was immediately present in the residue left after solution of those limestones. It is expected that weathering was intense in the Missouri area during Cheltenham time since the climate was favorable for the growth of luxuriant vegetation (coal) which implies abundant moisture. Rain water moving through the ground would become mildly acid from CO_2 (decomposing vegetation) and weak organic acids; this would have tended to weather the residual clay to the kaolinite stage (Ross, 1943). Some illite might escape alteration, however, and be carried into the Cheltenham swamp pools to remain unchanged, for it now occurs in the semi-plastic fire clay.

Continued leaching and removal of Na^+, Ca^{2+}, Mg^{2+}, and K^+ ions from the parent clay substance must have occurred to provide for the notably low content of the Cheltenham fire clay in those fluxes. In the high alumina clays, silica must have been dissolved away from the clay gel in the marshes. It is logical that the leaching and removal was upward, by dialysis and diffusion down the concentration gradient, but upward into the fresher water and more dilute solution on the tops of the pools and swamps. Abundant rain falling directly on the swamps, and/or fresh water from run-off of the land flooding over the swamps, could readily have flushed off the top solutions of cations and renewed the fresh water on top of the marsh pools, thereby accelerating and maintaining the upward dialysis process. If the climate in Cheltenham time was like present-day tropical rain-forest climate, and the presence of coal is suggestive of it, the mechanism of upward dialysis into fresh rain water would have been efficiently possible.

By this mechanism of cation removal, the purity and refractoriness developed in each clay pit or clay layer would have been a function of the rate and thoroughness by which the clay was locally refined or dialysed — following, of course, the inherited composition of the original sediment. Within the dialyzed clay gel and hydrated oxides, crystal aggregates could have grown in criss-cross random patterns. Considerable variation between basins of clay would be expected in terms of content of quartz sand, iron sulfide, plant residues, and clay content, and in their dialysis. Such variables explain the differences in clay pits previously described.

Seaward from the belt in which this semi-plastic fire clay was originating, a typical marine shale would be expected as a deposit. Such a facies change occurs and explains the disappearance of fire clay down dip from the Ozark Dome and the occurrence of shale in the extension of the fire-clay stratigraphic zone.

Concomitant with the facies change is a thickening in wedge form of the stratigraphic section between the Cheltenham and Fort Scott formations. On Goerlich Ridge, in the diaspore region south of the Missouri River, a thin (about 6 inches) shale lies between the Cheltenham clay and the Fort Scott limestone; 50 miles to the north, in Callaway and Audrain counties, 50 to 70 feet of sediments, allocated to the Loutre, Tebo, Ardmore, Bevier, and Lagonda formations, intervene between the Cheltenham and Fort Scott; and farther north and westward in central Kansas about 200 feet of sediments occupy the same stratigraphic interval. Obviously a structurally negative element was sinking farthest from the Ozark Dome. The sinking was rapid enough to prevent the dialysis of deposited sediments in a fresh-water environment, and therefore no economically usable fire clay (low in alkalis and alkaline earths) was produced. Tectonics and sedimentation, this far down the Dome, were not of the type to allow the development of fire clay.

The Flint Clay Belt

In a southerly, up-dip direction from the belt of semi-plastic and semi-flint clay toward the Ozark Dome, we first find the belt of soft and hard flint clay and then the belt of flint and diaspore. Although each type of fire clay is characterized by distinctive physical and ceramic properties, there is a continuous series between the types. Similarly, belts of the particular clay types are not separated by sharp boundaries, but in a general way are zoned as shown in Figure 4. The soft and hard flint clays in the belt from Fulton, through New Florence to Warrenton and Wright City, are blanketlike in occurrence, as are the occurrences of the semi-plastic clay layer, but because these flint clays were raised slightly higher on the flanks of the Ozark Dome, their former cover of overlying Pennsylvanian rocks was more nearly removed by pre-Pleistocene erosion (peneplanation). Consequently, in some flint-clay localities the upper and continuous part of the clay blanket was deeply or entirely eroded, leaving behind only the clay that had filled the deeper basins. These deeper basins are found now as single, isolated pits on the margins of severely eroded

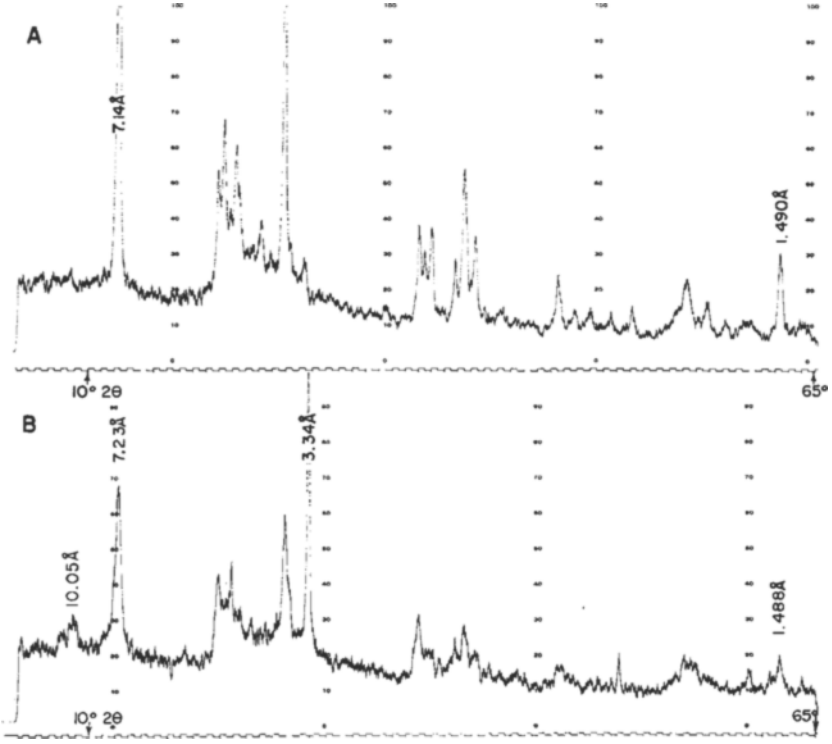

FIGURE 2. — X-ray powder diffractograms of (A) the flint clay from the Bueker pit, and (B) semi-plastic fire clay from the upper layer in the Hook-Leader pit of the Mexico Refractories Company. Noreclo x-ray, Ni-filtered, Cu K_α radiation.

flint-clay districts. Where Pleistocene erosion was minimal, as in the north side of the New Florence and Warrenton districts, continuous and thicker clay zones are present.

Mineralogically, Missouri hard flint clay is essentially kaolinite in very fine grain, as is shown by x-ray diffraction powder diagram (Fig. 2) and differential thermal analysis. Anatase found in Missouri fire clay (Hanson, 1953) probably accounts mineralogically for TiO_2 which commonly runs high in chemical analysis (see analysis no. 2 in Table 1).

Soft flint-fire clay commonly contains illite which may be concentrated in the fine-grained fractions of aqueous suspensions of the clay. Probably the illite is interstitial to, or coats particles of kaolinite. We do not ascribe all of the softness in soft flint clay to illite admixture; the factors which control flint-fire-clay textures and lithology are still not completely known. Differential thermograms of soft flint clay ordinarily show less intense thermal responses which occur at slightly lower temperatures than do those of hard flint clays or of relatively pure, coarsely crystalline kaolinite.

Flint-clay deposits may range in color from coal black (owing to an abundance of carbon) to popcorn white (the "popcorn" flint clay of the miners is light-colored, hard, and breaks into small fragments bounded by conchoidal surfaces). Pyrite is scantily present in Missouri flint clays. From the coal and sparse pyrite, it may be inferred that a negative Eh prevailed in the basins where Missouri flint clays were being formed.

Because the chief mineralogic differences between flint and semi-plastic clays of the Cheltenham are a decrease in illite and better crystallinity of the kaolinite in flint clay, it is inferred that the flint clay originated in a chemical environment of higher H^+ ion concentration and lower K^+ ion concentration. Geologically, the flint clay belt is in the proper location to have occupied a more stable land area than that required for the formation of the semi-plastic clays.

In summary, we infer that Cheltenham flint-and semi-plastic clays developed from essentially the same clay source, but that flint clays were formed where dialysis and leaching were more prolonged or where acidity was higher, owing to a position on a more stable land mass so far from and so constantly high above the ocean that marine water and salts did not enter the marshes in influential quantity.

The Diaspore-Clay Region

Occurrence of the clay pits (deposits). — The diaspore (and boehmite) and the so-called "burley" clays (those which are intermediate in chemical and mineralogical composition between flint clay and first-grade diaspore) occur closest to the summit of the Ozark Dome. Likewise, the diaspore clays are highest of all in alumina content (see analysis no. 1 of Table 1), and therefore leaching of silica, and/or concentration of alumina were highest. A close correlation between occurrence and composition of the diaspore clay is inferred.

Most of the diaspore pits (deposits) occur in single, separated, funnel- or chimney-shaped cavities 25 feet to perhaps 300 feet in diameter, and range to more than 200 feet in depth. They have been dissolved out of the Jefferson City and Gasconade dolomite country rock. Many pits are no larger than 75 feet in diameter and 50 feet in depth. Because most of the deposits were found in single occurrences (some in "twins"), an idea developed locally, and has been held tenaciously, that diaspore and associated flint clay deposits were formed solely in individually isolated solution pits and collapsed sinkholes. Only within the last 5 to 10 years has evidence been uncovered which shows that the older idea was based on incomplete evidence, and so gives only part of the story.

Within the last decade extensive mining operations on Goerlich Ridge between Drake and Owensville, in the vicinity of the Bueker-Farnberg-Aufderheide properties, have exposed within a single clay pit the undisturbed sequence of rocks from the Cheltenham to the Fort Scott formation above (see the Stratigraphic Section). In this local area, therefore, where

PLATE 3. — Relatively shallow basins which contained flint and diaspore clay on Goerlich Ridge, near the Bueker pit.

erosion has not removed its cover, the upper part of the Cheltenham is preserved as it occurred in Paleozoic time, and the geologic history of the diaspore region, through Fort Scott time, is recorded in its beds. In this region wide, shallow deposits of clay occur in more or less continuous, irregularly connected, broad, shallow basins just like those in the semi-flint and flint-clay regions to the north (Pl. 3). The physiography of the two regions must have been much the same — indeed, it was only one basin of sedimentation, and the concept of "two" regions arose from an artificial classification.

The origin of single, deep diaspore pits is also explained from the geologic record on Goerlich Ridge. Within the assemblage of surrounding shallow deposits on the Ridge, the deep Farnberg pit extends to a depth of more than 100 feet (Fig. 3). If erosion had removed the shallow clay here, the deeper Farnberg deposit would have become an isolated pit. By applying this explanation to the entire diaspore region, it is manifest that most of the fire clay originally present in the diaspore region has been eroded, and that only the erosional remnants, buried outliers, still remain for possible exploitation by mining.

The sinkhole structures are of various types. Some of them were formed by the collapse of their roofs, and others by widening of joints. Some of them had been formed before Cheltenham deposition started, others began (and many continued sinking) during the time interval of Cheltenham deposition. Evidence for the latter kind is a synclinal structure in pits whose topmost layers thicken prominently toward the center (the center of the floor was sinking while filling kept pace on top). Some shallow basins were filled with clay initially, and their floors later collapsed

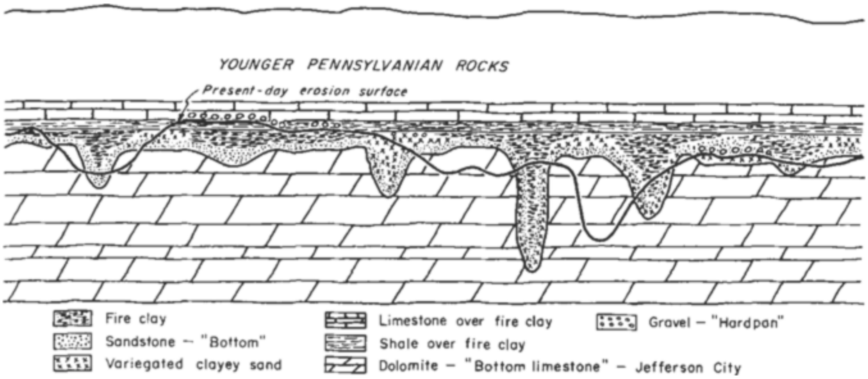

FIGURE 3. — A diagrammatic cross section through a part of the diaspore-flint clay district of Missouri. The complete section shows the stratigraphy as it occurred at the Bueker pit shortly after deposition of the Fort Scott limestone (the limestone shown over the fire clay).

The heavy line which cuts irregularly across the dolomite and the overlying rocks (Pennsylvanian) represents the surface of the land today. The presence of a few erosion remnants of gravel, shown in two places, indicates prior erosion followed by deposition of a sheet of gravel, and subsequently renewed erosion.

Below the present erosion surface are found Pennsylvanian sediments barren of fire clay, shallow deposits of fire clay, and a few deep deposits filled with fire clay and/or sandy, "worthless" clay. The deep deposits are preserved as buried erosion remnants. They may be surrounded by Pennsylvanian rocks or by Ordovician dolomite, depending upon the vagaries of erosion as occurred in Cheltenham and Recent times.

into caverns beneath. This resulted in an almost monoclinal, hinge or "trap-door" structure, which has been described by McQueen (1943).

Although erosion has removed most of the fire clay that was originally uppermost in the diaspore region, Pennsylvanian sandstone and clayey sand commonly remain as country rock surrounding the deep clay-pits. These sediments are important clues to the prospector, who has a statistically better chance of finding a clay pit if he hunts within an area that is surfaced by the Pennsylvanian rather than by older rocks. The possibility is not ruled out, however, that the bottom remnant of an unusually deep pit may be found entirely surrounded by Ordovician dolomite with no Pennsylvanian rock nearby. Examples of such pits are the one just south of Aud post office, and the recently discovered (1952-53), very deep pit within the Gasconade dolomite near the Meramec River below Meramec State Park. Moreover, remnants of deep pits of this type occur at considerable lateral distances from the center of a rich, clay-producing district. A wide range in the size, depth, shape, and areal distribution of clay pits may be found between regions of the type on Goerlich Ridge, and those on the very fringe of clay pit occurrences.

Mineralogy of the diaspore clay deposits.—Mineralogically, the diaspore-clay deposits are composed of diaspore and kaolinite which is fairly well crystallized. Boehmite occurs in place of diaspore in a few of the deposits. Both goethite and lepidocrocite, and probably anatase (because TiO_2 is prominent in chemical analyses) are also commonly present (see Analysis no. 1 in Table 1). Between end members of relatively pure diaspore ("first-grade diaspore" requirement long stood at 70 percent Al_2O_3, but has been relaxed to 65 percent) and relatively pure flint clay (chemical composition equaling that of kaolinite) lies a complete range of mixtures of the two clays. These mixtures have been named "burley flint," "burley," "burley diaspore," and "second-grade diaspore," and other terms which are useful for particular purposes. Burley clay takes its name from the "burls" (a miners' term for oölites); most of these oölites are rich in diaspore, Plate 4, but diaspore may also occur as fine, disseminated grains intermixed within the flint clay matrix. First grade (relatively pure) diaspore may likewise have oölitic or grainy ("mealy") textures.

Gibbsite has not been found in Missouri high-alumina clay. Allen (1935; 1937) reported an occurrence of it but was later unable to confirm the identification (personal communication, 1951) and questioned his earlier determination. We have not detected any gibbsite and we attach

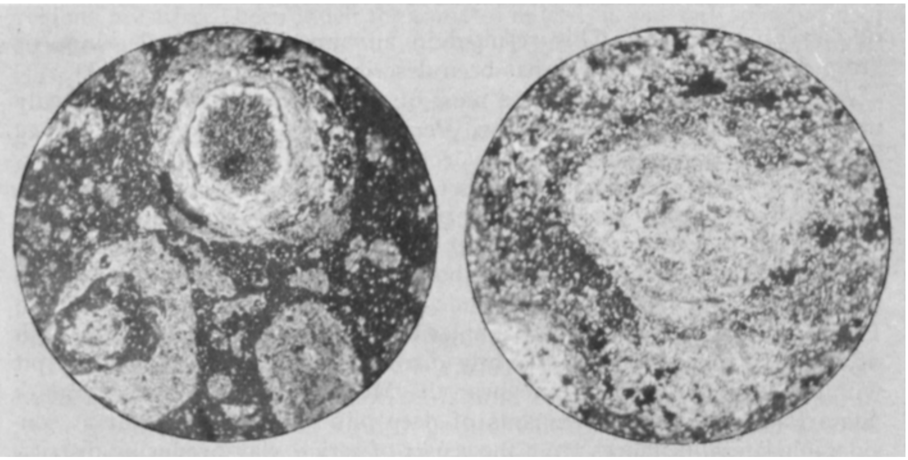

PLATE 4. — Photomicrographs of oölites and tiny grains of bright birefringent diaspore in association with low birefringent flint clay (kaolinite). Disseminated grains of diaspore, and concentric layers of diaspore in oölites are observable. Crossed Nicols, original magnification 50 x.

genetic significance to its absence. Under present-day weathering, gibbsite is developed under conditions of severe downward leaching (transportation implied) at the surface where oxygen is in excess. The association with diaspore of coal, pigmenting organic carbon, and very rarely pyrite, is good evidence that diaspore was formed under reducing conditions. Diaspore and boehmite may be indicator minerals of a reducing, water-logged genetic environment, whereas gibbsite (and laterite) indicates leaching by freshened, circulating water under oxidizing conditions.

Oölites (Pl. 4) of diaspore may have developed directly from a gel state, in accordance with observations that concretionary structures are readily derived from colloidal gels. Granular texture in diaspore commonly shows a textural transition to adjacent flint clay, similar to typical replacement texture, and this relationship may have originated either by replacement or reconstitution. That diaspore grains in the clay are definitely not detrital is shown (1) by mutually indenting boundaries between diaspore and flint or burley clays at any angle to the horizontal, (2) by continuously gradational boundaries between them, and (3) by fine textural (microscopic) details which are utterly unlike the contacts of detrital particles.

An hypothesis of hydrothermal origin for diaspore. — Missouri diaspore probably originated under low temperatures as did most sediments. The possibility, however, of a hydrothermal origin should be explored, particularly in view of the stability relations found in the laboratory for the system: Al_2O_3 - H_2O. Ervin and Osborn (1951) competently studied this system and found the stability field of diaspore to be higher in temperature and pressure than is consistent with the observable field relationships of Missouri diaspore. They state (1951, p. 390):

> Therefore, in this respect the equilibrium diagram can be applied directly to field occurrences, and the most important conclusion about diaspore origin is that, if the diagram is correct and if diaspore crystallized as a stable phase, diaspore must have formed under hydrothermal conditions, that is, at a temperature above about 275° C. and a (steam) pressure of at least 2,000 lb/in^2, or 130 atm.

They further state (p. 392)

> On the basis of the equilibrium diagram of figure 1 [figure 1 of Ervin and Osborn] and a consideration of the other types of occurrence of diaspore, it would appear that the gibbsite or boehmite was converted to diaspore as a result of the application of heat and pressure. The diagram indicates a minimum pressure of about 2,000 lb/in^2, corresponding to a depth of burial of about ½ km., for the stable crystallization of diaspore. It seems reasonable that diaspore deposits such as those in western Pennsylvania were buried as deep as that. The only question, then, is temperature. If burial of these aluminous deposits has not been sufficiently deep that temperatures of the order of 275° C. were reached as a consequence of normal geothermal gradient, then there is still the possibility of penetration by hydrothermal fluids or the close approach of igneous rocks to supply the required heat. . . .
>
> Diaspore might conceivably form in nature under conditions of temperature and pressure where it is not a stable phase, as, for example, at low pressures and at temperatures below 275° C. But this is very unlikely in view of the diaspore-boehmite density relationship and the ease with which gibbsite and

> boehmite form in this range, coupled with the difficulty of forming diaspore even under conditions at which it is stable. Furthermore, if boehmite is present, this cannot be converted into metastable diaspore. Diaspore can form from boehmite only if the pressure and temperature are increased to the point that diaspore is the stable phase. If the structure of diaspore contains sufficient quantities of other ions in the Al^{3+} positions, such as Fe^{3+} or Mn^{3+}, then this structure may be stable at lower pressures and temperatures than pure diaspore, but probably only a trace of other ions occurs in the diaspore of bauxite and diaspore clays.

Analysis no. 1 of a typical Missouri diaspore clay does not show a particularly large amount of nonaluminous trivalent ions. Geologic evidence does not provide a source of high temperature. Igneous rocks are not exposed in the diaspore district of Missouri, and no indirect evidence of their formation or of their association with the fire clay is known.

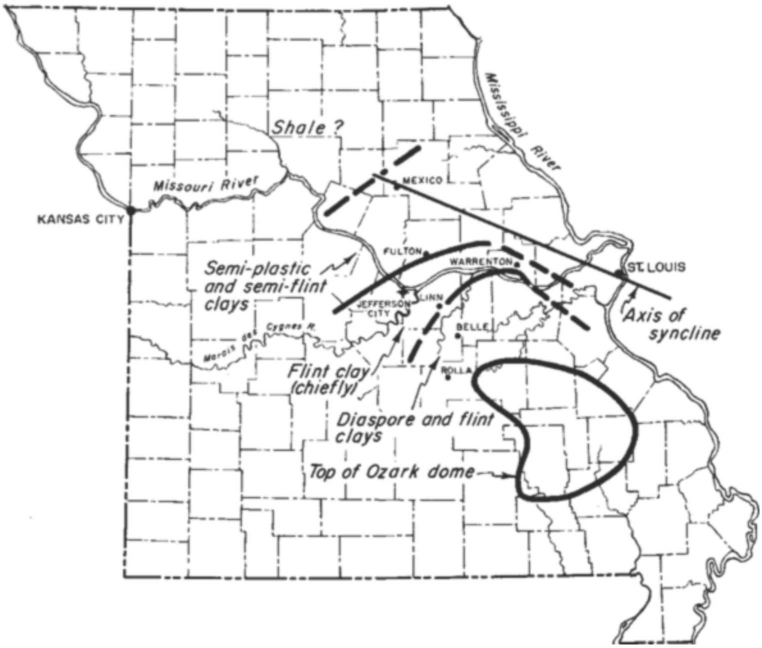

FIGURE 4. — Map of Missouri showing belts within the Pennsylvanian rocks which are characterized by particular clay types, *i.e.*, litho-facies types within the Cheltenham. The alumina content of the clays typifying each band increases progressively toward the apex of the Ozark Dome. The belts are roughly concentric in the northwest sector of that flank of the dome, and they terminate where erosion has removed the Pennsylvanian.

The axis of the syncline in which flint clay, semi-flint, and semi-plastic fire clays were preserved is shown between St. Louis and Moberly. The more plastic fire clays occur lowest in the syncline; flint clay occurs in the northeast flank (Whiteside locality) where the rocks rise on the Lincoln fold, and toward the south where they were raised by the Ozark doming.

About 50 to 70 miles southeast of the diaspore region, diatremes of post-Devonian age (Tarr and Keller, 1933; Rust, 1937) are known but there is no geologic evidence, direct or indirect, that any of them occur in the fire clay fields. As to the effect of possible hydrothermal solutions supplying heat to Missouri diaspore (following the suggestion of Ervin and Osborn), we question the probability of their being important, although they were considered by the late Professor W. A. Tarr.

After the passing of Professor Tarr in 1939, Mrs. Tarr kindly turned over to Keller many of Tarr's notes, among which were some on "The origin of Missouri clay deposits," dated January 18, 1926. Herein, in Prof. Tarr's own writing, are listed the following notes, quoted verbatim, which outline, on possibly permissive evidence, a mechanism by which hydrothermal solutions might have played a role in the origin of Missouri diaspore. Whether or not Prof. Tarr subscribed in later years to this mechanism is not known. It deserves attention and review, and has not been published before.

From Prof. Tarr's notes:

> "Origin of Missouri clay deposits"
>
> 1. They are due to leaching by warm solutions, rising from below.
> 2. These solutions contained much H_2S as is shown by the association of *pyrite* [Tarr's italics] with the leached clays.
> 3. Pyrite is found everywhere at the contact of the Pennsylvanian and Mississippian, or at slightly higher levels in the Pennsylvanian.
> 4. This pyrite and the clay are found mainly in association with solution cavities in the Mississippian limestone (also Jefferson City dolomite) [Tarr's parenthesis].
> 5. These channels in the Mississippian were followed by the solutions rising from below.
> 6. The solutions attacked the clays in the channels, or spreading along the lower portions of the Pennsylvanian, especially in sandy phases of the clays, leached the clays with the following results.
>   a. They removed the more soluble and fluxing materials, CaO, K_2O, Na_2O, FeO, MgO, thus producing a high grade *fire clay*.
>   b. They leached silica from the clays, thus raising the alumina content.
>   c. In special cases they not only leached the silica, etc., but were hot enough to form diaspore, a mineral heretofore found only in high-temperature or metamorphic rocks. . . . This origin by hot solutions explains the presence of the diaspore, a mineral not formed by lateritic weathering as some have sought to explain these clay deposits.
>   d. An accompanying result was the deposition of pyrite (and marcasite), and more rarely, sulfides of lead and zinc.

The reasoning of Tarr, quoted above, is offered as possible geologic support furnished by Missouri fire clay (especially diaspore) for the laboratory work of Ervin and Osborn. We believe that Prof. Tarr's thesis is not tenable in the light of more recent geologic evidence uncovered, and we do not see how the clay deposits could have been subjected to a temperature of 275°C. Aside from detailed, positive geologic evidence (specifically in the Bueker pit) contrary to a high-temperature origin, the following general considerations argue against it.

1. A high temperature, 275°C (or higher), and high pressure, which would have been compatible with phase-rule requirements for the deposition of stable diaspore, or the conversion of boehmite to diaspore, probably would have been accompanied by recrystallization of the ultrafine-grained flint clay to coarser kaolinite, or to dickite. Whereas all dickite genesis is not necessarily restricted to hydrothermal action, clay minerals of the kaolin group which have a hydrothermal history are, in many cases, dickite or nacrite. Dickite has been found in Missouri rocks within the general clay region, but in rocks lower stratigraphically than the Pennsylvanian (Tarr and Keller, 1936). The rocks in which diaspore was formed do not carry dickite.

2. If high temperature and pressure (as required by Ervin and Osborn) had prevailed, we would expect changes in the country rock, such as recrystallization in the dolomite, and silicification and pronounced induration in the sandstones, sands, and shales adjacent to diaspore deposits. The dolomite in the Jefferson City formation is no different around a diaspore deposit than it is a hundred miles away from the diaspore region. Poorly indurated sand and friable sandstone are brought up by prospect drills, alongside, and over, diaspore deposits; whereas hydrothermal action, if involved, would have changed some of those arenites into quartzites.

3. In a fire-clay-producing region approximately 50 kilometers north of Mexico City, Mexico, hydrothermal solutions have risen through the rocks and have leached silica from them, with the result that fire clay deposits have been developed there. The evidence for hydrothermal action is unmistakable, and a wide-spread layer of opaline, chalcedonic, and siliceous sinter occurs in varying thicknesses over and adjacent to the clay pockets. The silica mantle is not something that might escape attention, because the silica rock, if present, would be penetrated en route to the clay. Westcott, who has examined hydrothermal clay occurrences in Mexico, finds nothing in the Missouri geology to resemble even remotely the hydrothermal occurrence.

4. Cannel and sub-bituminous coal have been mined from diaspore pits, but these coals appear to be no different from the coal found in sinkholes 50 miles north of the diaspore region. No evidence of heat effects, hydrothermal action, or metamorphism on the coal is evident.

5. The abundance of pyrite (and marcasite) in fire clay, on which Tarr's theory largely depends, is true only for the semi-plastic and semi-flint fire clay, where the degree of alteration has actually been the least. In the flint-and diaspore-clay deposits, where the alteration, as postulated by Tarr, has been the greatest, pyrite is scarce. Tarr's hypothesis, therefore, is vulnerable to restrictive evidence which has appeared as a result of recent observations, and Ervin and Osborn's excellent chemical laboratory work is not supported by geologic field evidence from Missouri diaspore deposits. We will suggest how the apparent disagreement between labora-

tory data and field evidence may be resolved after proposing a low-temperature origin for the diaspore.

Low-temperature origin of the diaspore clays. — Prior reference has been made to our belief that the diaspore clay originated under the ordinary low temperature of surface sedimentation, and that the field evidence found in the Bueker pit is significant. The Bueker pit, which is a large, shallow-basin type of mixed flint, burley, and diaspore clays, has been opened to an area of about 150 by 225 feet and to a depth of about 35 to 40 feet. Flint clay is most abundant in it, but considerable burley clay, ranging up to and including some first grade diaspore, is present. Diaspore and burley clays show gradational contacts. Stratification, which is based on color differences in the clay, on partings, and on differences in clay-mineral composition (diaspore to kaolinite of flint clay), carries continuously across only part of the pit, owing to overlap by other beds. These layers and color bands show a slight synclinal structure in the pit, due probably to solution of the underlying limestone and perhaps some differential settling. The same description, with slight modification, applies to most of the diaspore deposits in the region. In other words, the Bueker pit is a typical, shallow, mixed deposit, perhaps slightly larger than the average, but otherwise representative of the flint-diaspore deposits in the district.

Lenticular layers of diaspore and burley clay occur in the lower two-thirds of the deposit and dip gently toward the center. Flint clay extends across the top of the pit, becoming as much as 20 feet thick in some places. This flint clay is first-quality, clean, light-colored, hard, and fresh, except in an oxidized zone, two to six feet thick, which occurs at the very top of the flint clay. In this oxidized zone the flint clay is soft, shelly, discolored (yellowish brown), and weathered. It can hardly be distinguished lithologically from weathered flint clay which is exposed to present-day surface-weathering conditions. Its lower contact with the fresh clay is typically gradational and undulating (thereby accounting for the variation in thickness). It is concluded that a zone and surface of ordinary weathering have been developed on top of the Cheltenham flint clay despite the fact that it is covered by younger sediments.

The significant relationship of the weathered zone is that it is overlain by a *fresh* and *unaltered,* phosphatic, grayish green, thinly laminated shale with which it is in razor-sharp contact. The clay mineral in the green shale is dominantly illite, whereas only one-half inch below, in the oxidized flint clay, the dominant mineral is kaolinite. Well-defined x-ray powder diffraction patterns give positive, clear cut clay-mineral identification (Keller, 1952).

Above the shale lies a marine, fossiliferous, nodular limestone having a maximum observed thickness of about six feet. A thin zone, one to two feet thick, of weathered, dark, carbonaceous shale overlies the limestone on the north edge of the pit; elsewhere around the rim of the pit it has been eroded. The limestone contains marine fossils — brachiopods, corals, and foraminifera — from which a Fort Scott age is determined (by Searight, Thompson, and Unklesbay, in Keller, 1952, p. 120). That the phosphatic illitic green shale is also marine is reasonably certain.

The geologic history of the fire clay is so clearly recorded in this pit that it is interpreted with singular ease and high confidence. Beginning with the formation of diaspore, burley, and flint clays in the lower part of the deposit, the next event was the deposition of the thick flint clay which continues to the top. After the formation and consolidation of that clean, hard, flint clay a period of weathering occurred in which the upper part of the flint clay was oxidized as much as 6 feet in depth. The exact time of this period of weathering is not determinable, but it was obviously post-Cheltenham and pre-Fort Scott. Following the weathering of the flint clay, the greenish, illitic shale which grades upward into the marine Fort Scott limestone was deposited over the clay. There is little reason to doubt that the shale is also marine, and that the shale-limestone sequence records a marine invasion over the clay area.

Implications regarding the genesis of the fire clay based on exposures in the pit are as follows. First, the presence of fresh (unoxidized) green illitic shale in immediate contact with the underlying oxidized and weathered flint clay shows that there has been no significant chemical action (oxidation or leaching) by downward-moving, oxidizing, surface water since Fort Scott time. Therefore, the flint and diaspore clay can not have originated through leaching action of surface water after Fort Scott time. A theory proposing such a mechanism of leaching by surface water is untenable.

Second, where surface water did penetrate flint clay during either Recent or Paleozoic times it softened, oxidized, and colored the flint clay to the extent of its penetration. This reaction has left not the slightest indication that diaspore was formed by it. The zone of oxidation in the flint clay does not penetrate to the diaspore and burley clay below it. Therefore, downward-moving surface waters did not leach enough silica out of preexisting clay during Paleozoic time to convert the residue into diaspore. Downward-moving, surface, oxidizing waters were not significantly instrumental in the formation of diaspore either before or after the time the clay was deposited above the diaspore. Flint clay is notably impermeable, and tends to seal its interior from liquids present on the outside.

Third, the diaspore apparently was formed prior to being covered with flint clay. Thus its origin is syngenetic. The geologic evidence requires that the chemical and mineralogical changes which produced diaspore (and boehmite) took place during the filling of the basin or sinkhole.

In the light of stratigraphic evidence from the Bueker pit, from the testimony of the texture and structure of the clays, and in accord with the general geologic (physiographic, sedimentologic, and tectonic) setting, we infer the following origin for the clays in the diaspore district of Missouri.

Prior to the deposition of the oldest Pennsylvanian rocks, karst topography was developed on the surface of the cherty, sandy Jefferson City dolomite. Solution work dissolved out shallow basins, small sinkholes, and fewer very deep sinkholes and caverns. Insoluble, but intensely weathered and oxidized chert, tripoli, iron oxides, quartz sand, and some clay were shifted about and deposited by streams which left the variegated, tripolitic, clayey sand and sandstone widespread over the region. Solution of the underlying dolomite continued during the deposition of all Pennsylvanian sediments through the fire clay; basins were deepened, sinkholes were widened and deepened, and collapse of their roofs occurred as sand, sandy clay, and fire clay were deposited in them, (Fig. 3). Deep sinkholes were formed in the diaspore region because it stood higher in elevation owing to its location on the rising part of the Ozark Dome. Farther north, in the semi-flint clay region, the land was lower with respect to its drainage outlet and underground drainage was shallower — deep sinkholes were not possible.

Toward the latter part of the deposition of the variegated clayey sand the entire region (probably all of Missouri and adjacent areas) was lowered with respect to the ocean and sedimentation was affected as follows. Finer clay muds derived from the weathering of the limestones were no longer swept out, but because of lower stream gradients remained within the diaspore region. Vegetation increased in abundance (coal and carbonaceous clay) and the oxidation potential was decreased, eventually falling to a negative Eh in the depositional basins. Highly oxidized sediments gave way to those containing carbon, the original compounds of which are strong reducers (Zobell, 1947). This suggests a change of climate from alternating wet and dry seasons (intense oxidation) to frequent, regularly-occurring rainfall that caused plants to cover the land continuously and maintain continued reducing conditions. Vegetation held the clay against erosion, and the clay impounded pools of water — marshes and swamps. Increase in surface water tends to increase local rains. The effect becomes cyclic, with the end result that a marsh and swamp condition, similar to that postulated for the semi-flint and semi-plastic clay portion of the fire clay region, was developed in the diaspore area.

Some differences would be expected between the two clay districts, however. The diaspore country was farther from the ocean, and higher above it than was the semi-flint area to the north. Sedimentation was slower probably, therefore, and leaching of the clay sediment more prolonged in the diaspore area. This probably resulted in removal, first, of the alkali and alkaline earth elements from the clay, and then silica, whereby diaspore and boehmite were formed. Hydrolysis and dialysis of the silicates (kaolinite and others) are appealed to as mechanisms during leaching for the removal of alkalis and the separation of silica from alumina. These are diagenetic processes. Oölites of diaspore were formed, and apparently replacement of some clay by alumina took place during this interval.

The hydrolyzed and dissolved substances appear to have been removed upward rather than downward in forming diaspore. There is no geologic evidence of alkalis or silica having been carried downward; neither the clays nor the underlying sandstone or dolomite show an addition or incursion of silica or alkalis. The bottoms of the clay-containing basins became increasingly impermeable to downward movement of water as the thickness and dialysis of clay increased. The major part of the substances extracted by solution moved by dialysis and diffusion down the concentration gradient which was upward into the fresher surface water. They were flushed away from the surface. This is the same mechanism as that proposed for the purification of semi-plastic clay, but the process probably went to a more advanced stage in the diaspore district because there the rate of sedimentation was slower, time of leaching longer, and the concentration of H^+ ions greater. In the semi-plastic clay district, the land was lower and sinking faster (stratigraphic evidence has been given) so more clay which had been less drastically weathered was brought in. Each increment of clay was covered by new clay before the older was completely leached, and the greater abundance of metal cations from the clay and some possibly blown in from the ocean maintained a higher pH; all of which operated against the alteration of the mud to hard flint clay or high-alumina minerals.

The transition in sedimentation in the Missouri diaspore district from sand and clayey sand to fire clay has been described. This change in sedimentation does not appear to have been abrupt vertically or horizontally. Moreover, most of the fire clay sedimentation apparently took place more prominently in some parts of the diaspore district than in others, and apparently began in different times in different places, and extended over longer periods in some localities than in others. Fire clay sedimentation probably never was continuous and did not form an uninterrupted blanket condition over the whole diaspore district at one time. The deposits appear to have been prominent locally, but elsewhere hardly occurrent, just as coal lenses thicken, thin, and disappear in Pennsylvanian sediments of the same age.

From the viewpoint of lithofacies and environments, we regard the diaspore to be a response of clay substance to prolonged and intense leaching and dialysis under water-logged, reducing, and slightly acid conditions, in a karst terrain relatively far from the ocean. Where the land was lower, sedimentation more rapid, and leaching less intense and less prolonged, softer flint clay was formed. Still nearer the ocean, under conditions of higher pH and higher concentrations of metal cations, and where sinking of the land accompanied sedimentation, a facies of semi-flint to semi-plastic clays was the clay product. Under a marine environment beyond, a typical marine shale is to be expected. We interpret the Missouri fire clays, therefore, as lithofacies changes in the Cherokee sediments.

The principle of structural and energy inheritance. — The explanation of the origin of Missouri diaspore at low temperature as postulated in this paper is, at first thought, in conflict with the findings of Ervin and Osborn. Upon further consideration, however, two mechanisms for the formation of the diaspore at low temperature, which leave compatible both low and high temperature syntheses, suggest themselves. In the first alternative, Missouri diaspore may have been deposited metastably, as has been suggested by Osborn (personal communication, 1953), and by Roy (personal communication, 1953), whereupon there is no conflict with its being stable at temperatures above 275°C.

In the second alternative, the structure and energy inherited from the parent kaolinite may have implemented the process by which diaspore could form with relative ease at low temperature. This mechanism invokes the principle of structural inheritance (Johns, 1953; Bradley and Grim, 1951; Frederickson, 1953), to which is added energy inheritance.

In the genesis of Missouri diaspore, the parent kaolinite is envisaged as undergoing hydrolysis and dialysis mildly, slowly, and quietly, without alternating periods of drying, and under conditions close to, if not actually of, reversibility. Under this environment the silica would be removed from the kaolinite lattice so gently during hydrolysis that it would leave the previously organized or ordered sheet of alumina octahedra ready to go directly over into diaspore (or boehmite) without the demand for high energy (high temperature and pressure) as required in the synthesis of Ervin and Osborn. Ervin and Osborn used as parent aluminous material relatively disorganized hydrated alumina which must surmount an energy barrier (so we speculate) in order to go to the ordered bonding in diaspore. On the other hand, if our inference about the inheritance of structure and energy from kaolinite is correct, diaspore formation at low temperature is entirely compatible with a high-temperature synthesis of it from more primitively organized materials.

When hydrolysis of clays or other silicates takes place under conditions of weathering such that the alumina and silica are transported (in either colloidal or molecular solution) for appreciable distances, as in laterization, the parent structure is broken up and disorganized (entropy increased) so drastically that the alumina, upon drying or crystallizing, forms gibbsite, but not diaspore. Gibbsite does not require for its formation from a precipitated gel the energy intensity from its surroundings that diaspore does (Ervin and Osborn, 1951).

We find the implications of structural and energy inheritance to accord with our reasoning from field evidence on the origin of diaspore and boehmite. Apart from the problem at hand, we endorse Johns' (1953) proposal that "the same principle governs, or at least influences, many reactions involving geologic materials," and believe that a similar implication in Frederickson's (1953) comments on the genesis of various minerals is potentially fruitful of many important geological applications.

Boehmite

Boehmite, the dimorph of diaspore, occurs less abundantly in the high-alumina clay region of Missouri than does diaspore, but has been produced there in commercial quantities from a few pits. Ordinarily it is intimately mixed with kaolinite, and therefore the boehmite-containing clay seldom is high enough in alumina, in large quantity, to meet 70 percent Al_2O_3 specifications. Boehmite clays in Missouri are commonly fine-grained, flintlike, compact, and relatively nonporous. Boehmite-containing clay resembles flint clay and some burley flint clays so closely in physical appearance that it may be unrecognized and pass for flint clay in some mining operations.

Diaspore and boehmite are also intimately associated in Missouri clays. Both have been identified, along with kaolinite and a chloritic mineral, in the powder from a single tiny sample no larger than ¼ inch long on a side (Keller, 1952, p. 125). They occur also in layers, which look like sedimentary beds, separated by a sharp, paper-thin parting (Keller, 1952, p. 127). Hence, both sharp and gradational contacts occur between diaspore and boehmite.

The origin of boehmite as distinct from diaspore in Missouri clays is not understood by us. Herold (in McQueen, 1943, p. 238) quotes de Lapparent (1936) as believing that the high-alumina clays of Ayrshire were formed by the hydrolysis of basalt whereby alumino-siliceous gels were released. Where the gels were flooded with humic waters boehmite and kaolinite were developed. Where the gels did not react with humic waters the hydrated alumina remained intact until rising isogeotherms converted the remaining aluminous gel into diaspore. In other words, the presence or absence of humic waters determined respectively whether boehmite or diaspore was formed. Because we find diaspore closely associated with abundant organic carbon in the Missouri clays, de Lapparent's hypothesis apparently does not explain the interrelationship of Missouri diaspore-boehmite.

Bridge (1952, p. 212) observed that the bauxite deposits of southern Europe contain boehmite as the principal aluminous mineral, whereas diaspore deposits appear to be confined to rocks of Paleozoic age. Ervin and Osborn (1951) found gibbsite to be stable at temperatures below 130°C and at pressures of about one atmosphere; boehmite was the stable hydrated alumina up to 275°C and 130 atm. pressure; and diaspore was stable above the range for boehmite. Could the high-alumina clay in the Missouri deposits have been boehmite originally, and have inverted to diaspore through long geologic time, in keeping with Bridge's observation? To this point, Ervin and Osborn (p. 392) state, "Diaspore can form from boehmite only if the pressure and temperature are increased to the point that diaspore is the stable phase". Arguments against the rise in temperature of the Missouri diaspore deposits to 275°C, have been presented and it appears doubtful that the diaspore originated from boehmite at 275°C.

We have done only a very small amount of detailed work on diaspore-boehmite field relationships and that has been insufficient to yield results of positive significance. Diaspore is characteristically more porous than boehmite, which has been observed only to be compact and "dense or tight". If boehmite inverted to diaspore after burial it would have had to decrease notably in volume to account for the increase in porosity. Measurements on the clays are not available, but it is doubtful that an increase in density from about 3.0 of boehmite to about 3.4 for diaspore (Ervin and Osborn, p. 387) will account for the increased porosity. Boehmite has never been observed in oölitic texture, and it is doubted that fine-grained boehmite would invert to oölitic diaspore, or to oölites comprised of concentric layers of diaspore and flint clay.

Obviously information about the field occurrence of boehmite in Missouri is too scanty to give basis for holding strong views on its origin, but what little we have seen of it does not support the origin of diaspore from pre-existing boehmite.

Sediments Overlying the Cheltenham Fire Clay

A discussion of the sediments which overlie the Cheltenham fire clay may be anticlimactic to follow a theory of origin of the clay, but for the sake of completeness a brief description of them is included. In the districts south of the Missouri River erosion has removed all of the Paleozoic rocks which originally overlay the fire clay except on top of Goerlich Ridge. Besides the green shale and Fort Scott limestone at the Bueker pit, local lenses of sandstone occur over the clay to the east.

Overlying the Pennsylvanian sediments is a layer of poorly sorted, rudely bedded and cross-bedded, subrounded to rounded, oxidized chert gravel with pebbles ranging generally from one to two inches in diameter. This layer of gravel (the "hardpan" of the prospectors and miners) is apparently continuous for several miles on Goerlich Ridge, where it reaches a maximum measured thickness of 30 feet on the August Heidbrink farm northeast of Owensville. It is encountered during prospecting at many places on high land between Owensville and Belle, and thence south to Vichy. It is likewise found on the high flats northeast of Linn (Osage County). At the Gaume pit near Aud (northeast of Linn) slabs of silicified limestone and chert boulders more than 2 feet in cross section are fairly common. The age of this gravel layer is not proved (Lafayette?), and the way it has been deposited has not been entirely solved. An opinion expressed by E. D. McKee,[1] who has extensively studied the Shinarump conglomerate and other nonmarine sedimentary rocks, is that the gravel

---

[1] Personal communication from Dr. McKee who visited the Heidbrink pit with the senior author, 1953.

resembles a typical deposit by streams which spread gravel into a body of shallow standing water.

Windblown soil, and colluvial or recent alluvial material, overlie the "hardpan" gravel and cover adjacent areas or intervening ones where the gravel has been eroded or not deposited.

North of the Missouri River, the Cheltenham fire clay is covered by succeeding Pennsylvanian formations, or where the latter have been eroded, by Kansan glacial drift and windblown soil.

SUMMARY

The genesis of the fire clay deposits of Missouri is examined from the approach of sedimentary petrology rather than from economic geology. That the fire clays of the Cheltenham formation, which are a part of the Cherokee Group (Pennsylvanian), are of economic value to man is only incidental to their genesis.

The several types of fire clays and the other associated sediments are considered lithofacies responses to variations in the environments of their deposition. The fire clays are sensitive indicators of environments so they may be used to interpret geologic history.

A newly opened diaspore pit (the Bueker pit) on Goerlich Ridge in the diaspore region between Drake and Owensville, Gasconade County, Missouri, contains an intact stratigraphic section from the fire clay up through the marine Fort Scott limestone. This is the first section known from a diaspore deposit in which Paleozoic rocks still cover the fire clay.

Geologic evidence seen in the Bueker pit shows that downward-moving, oxidizing, surface waters did not play a significant role in the leaching of clay to form diaspore. The flint and diaspore clay were developed to essentially the same condition in which they are seen today before the erosion interval which preceded Fort Scott deposition.

Geologic field evidence is contradictory to an origin for diaspore at the high temperature, 275°C, and high pressure, 130 atmospheres, at which it is stable under equilibrium conditions in the laboratory. It is suggested that the structure and energy of an octahedral alumina sheet are inherited from kaolinite or other clay minerals and the alumina octahedra are passed on without extensive modification to become diaspore, thereby meeting the energy requirements of the hydrothermal synthesis of diaspore.

The genetic relationship of boehmite to diaspore in Missouri high-alumina clays is not well understood.

The genesis of the Missouri fire clays is inferred as follows. During early Cherokee time the fire clay region was characterized by karst and solution-basin topography on the Jefferson City dolomite and the Burlington limestone. The land was low-lying, and near the sea at the north. The southern part was high and tectonically positive. When sinking occurred, the north and west parts sank more rapidly than other parts. Fine colloidal clay, along with silt, sand, and chert, derived from the

limestone and dolomite were deposited in marshes and swamps which filled the solution basins and sinkholes. This clay underwent dialysis in the basins of deposition, whereby fluxes and silica (especially in the diaspore district) diffused upward toward fresh surface water and were flushed away. The leaching was relatively more prolonged and more intense in the southern part of the clay region where high-alumina clays were developed. In the northern part — the semi-flint and semi-plastic fire clay district — sedimentation was more rapid, leaching was less intense, and therefore kaolinite and some illite were developed. The Eh in all fire clay deposition and diagenesis was reducing; the pH was probably weakly acid in the south to perhaps neutral in the north. The fire clays which were formed indicate the range in environments of deposition. The single and isolated diaspore-flint pits in the southern region are erosional remnants (buried outliers) of deep sinkhole deposits which extended to depths below which present-day erosion has progressed.

ACKNOWLEDGMENTS

Mrs. W. A. Tarr and E. D. McKee kindly read the manuscript and offered many valuable suggestions. They are not responsible for any of its shortcomings, however. Automobile expenses for one trip to the diaspore region were furnished under University of Missouri Research Council Grant No. 478.

REFERENCES

Allen, V. T. (1935) *Mineral composition and origin of Missouri flint and diaspore clays:* Mo. Geol. Sur., 58th Bien. Rpt., App. IV., 24 p.

—— (1937) *The Cheltenham clay of Missouri:* Mo. Geol. Sur., 59th Bien. Rpt., App. V., 29 p.

Bradley, R. S., and Miller, B. K. (1941) *Prospecting, developing, and mining semi-plastic fire clay in Missouri:* AIME, Tech. Pub. No. 1328, 9 p.

Bretz, J H. (1950) *Origin of the filled sink-structures and circle deposits of Missouri:* Geol. Soc. Amer. Bull., v. 61, p. 789-834.

Bridge, J. (1952) *Comment in Problems of clay and laterite genesis, a symposium:* AIME, symposium volume on above title, p. 212-13.

Brindley, G. W., and Robinson, K. (1947) *Fire clay:* Brit. Ceram. Soc. Trans., v. 46, p. 49-62.

Davis, W. M. (1930) *Origin of limestone caverns:* Geol. Soc. Amer. Bull., v. 41, p. 475-628.

Ervin, G., Jr., and Osborn, E. F. (1951) *The system* $Al_2O_3 \cdot H_2O$*:* Jour. Geol., v. 59, p. 381-394.

Frederickson, A. F. (1952) *The genetic significance of mineralogy, and comments, in Problems of clay and laterite genesis, a symposium:* AIME, p. 1-11, 233-35.

Hanson, R. F. (1953) *A mineralogical study of selected raw and fired Missouri clays:* unpublished M. A. thesis, Univ. of Mo. library.

Ingram, R. L. (1953) *Fissility of mudrocks:* Geol. Soc. Amer. Bull., v. 64, p. 869-878.

Johns, W. D. (1953) *The mineralogy of flint clays and associated fire clays:* Thesis for the Ph.D., University of Illinois.

Keller, W. D. (1938) *Diaspore clay cast of wood in a Missouri diaspore pit:* Amer. Mineral., v. 23, p. 461-463.

—— (1946) *Evidence of texture on the origin of the Cheltenham fire clay of Missouri and associated shales:* Jour. Sed. Pet., v. 16, p. 63-71.

—— (1952) *Observations on the origin of Missouri high-alumina clays:* AIME symposium volume on *Problems of clay and laterite genesis,* p. 115-135.

——, and Westcott, J. F. (1948) *Differential thermal analyses of some Missouri fire clays:* Amer. Ceram. Soc. Jour., v. 31, p. 100-105.

McQueen, H. S. (1943) *Geology of the fire clay districts of east central Missouri:* Missouri Geol. Sur. & Water Resources, 28, 2nd series, 250 p.

Millot, Georges (1949) *Relations entre la constitution et la genèse des roches sédimentaires argileuses:* Bull. l'assn. ingen. geol. Univ. Nancy, Tome II, 352 p.

Muilenburg, G. A. (1953) *The mineral industry of Missouri in 1950:* Missouri Geol. Sur. & Water Resources, Inf. Cir. No. 9, 20 p.

Robbins, Carl, and Keller, W. D. (1952) *Clay and other non-carbonate minerals in some limestones:* Jour. Sed. Pet., v. 22, p. 146-152.

Ross, C. S. (1943) *Clays and soils in relation to geologic processes:* Jour. Wash. Acad. Sci., v. 33, p. 225-235.

Rust, G. W. (1937) *Preliminary notes on explosive vulcanism in southeastern Missouri:* Jour. Geol., v. 45, p. 48-75.

Tarr, W. A., and Keller, W. D. (1933) *A post-Devonian igneous intrusion in southeastern Missouri:* Jour. Geol., v. 41, p. 815-823.

—— (1936) *Dickite in Missouri:* Amer. Mineral., v. 21, p. 109-114.

Urbina, J. E. (1910) *Informe acerca de una excursion geologica preliminar efectuada en el Estado de Yucatan:* Parergones del Inst. Geol. de Mexico, Tomo III, Numero 7.

Van Hise, C. R. (1904) *A treatise on metamorphism:* U. S. Geol. Survey Monograph 47, 1286 p.

Wheeler, H. A. (1896) *Clay deposits:* Missouri Geol. Sur., Bull. v. 11, 622 p.

Zobell, C. F. (1947) *Studies on redox potential of marine sediments:* Amer. Assn. Pet. Geol. Bull., v. 30, p. 477-513.

DISCUSSION

H. R. Gault. — For what it is worth, I would like to mention, in support of Dr. Keller's theory, an occurrence of aluminum hydroxide. There is an abandoned coal mine in Pennsylvania where 18 inches of a yellow gelatinous substance has been deposited in old drifts in 80 years. The material is amorphous under x-ray spectrophotometer and contains about 48 percent Al_2O_3, 5 percent SiO_2. Loss at 900° was better than 50 percent. If this can happen in 80 years, perhaps Dr. Keller can make his diaspore in the time he has available without any upward solution.

I would also like to ask whether the time factor has been considered sufficiently by the laboratory people.

W. D. Keller. — More field observations like that of Dr. Gault will help us understand the origin and movement of aluminum hydroxide in the zone of weathering.

L. M. Sherman. — Dr. Bridge, in the Laterite symposium, remarked that diaspore was predominant in Paleozoic deposits, boehmite in Mesozoic deposits, and gibbsite in Cenozoic deposits. Here is a time factor. In the ceramic industry, a material may be fired at one temperature for a certain time, and next at a lower temperature for a longer time, with identical results. It seems possible that the 275° temperature requirement for diaspore, as determined by short-term laboratory tests, might be materially reduced as a result of the immense time involved.

W. D. Keller — Prolonged duration of reaction as a substitute, even in part, for higher intensities of temperature, chemical potential, etc., carries tremendous implications for geological phenomena. More sound information on the limits to which such substitution is effective is to be welcomed by the geologist not only on the problem of diaspore genesis but on many others in earth science. The occurrences observed by Dr. Bridge may have resulted because diaspore is more stable than gibbsite.

Rustum Roy. — I would like to say, as an experimentalist from the laboratory, that Prof. Keller's observations and deductions are most valuable since he has considered the possibilities suggested by laboratory evidence.

With respect to the objections raised by Prof. Keller to Tarr's unpublished hypothesis (and to the same idea of the possibility of the diaspore being heated above 275°C suggested by laboratory work) it must be pointed out that we have already dealt with two of the main objections cited. It was claimed that there was a lack of the usual signs of high-temperature treatment of clay bodies, e.g., the absence of nacrite or dickite; and it was suggested that the presence of other ions might lower the temperature of inversion of boehmite-diaspore.

We have dealt with both these problems experimentally. Hill, Roy and Osborn (J. A. Cer. S. 35, 135, 1951) have shown that even 15 mol percent Ga_2O_3 replacing Al_2O_3 causes a decrease of only about 10°C in the inversion temperature of boehmite to diaspore, so that the explanation based on impurities in the lattice cannot be used. Roy and Osborn ("Clay and Laterite Genesis," Symposium, A.I.M.E.) in their study of the system Al_2O_3-SiO_2-H_2O were unable to find any correlation between high temperature of formation and the presence of nacrite or dickite. Kaolinite can be synthesized even 5° below the equilibrium decomposition temperature for the $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$: hence, the absence of nacrite and dickite cannot be construed as evidence against possible heating up of the diaspore pocket. If there is no positive evidence for the presence of hydrothermal activity there does not seem to be any distinct evidence which would eliminate such a possibility.

W. D. Keller. — Dr. Roy finds geological field observations unconvincing that hydrothermal activity is eliminated in the origin of diaspore (in Missouri). A nonpartisan person might ask in a situation of this kind if the field geologist is convinced too easily by sheer weight of much field evidence which may be insufficiently restrictive in quality, or if the experimentalist, on the other hand, extrapolates laboratory-obtained data to unreasonable and invalid distances from a relatively simple laboratory system to a larger and more complex field system in which enter unrecognized variables that are beyond the conditions of his experiment? Experience has shown that defections in both approaches have led to erroneous scientific conclusions. The two perspectives afford healthy checks on each other and stimulate search for a more complete array of evidence. In the meantime, until evidence is overwhelmingly complete, difference of opinion is the logical outcome, and the observer not active in the problem may enjoy weighing for himself the data presented and drawing his own conclusions.