CLAY-MINERAL ENVIRONMENTAL RELATIONSHIPS IN CISCO (U. PENN.) CLAYS AND SHALES, NORTH CENTRAL TEXAS

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ABSTRACT

The clay-mineral composition of 142 samples of Upper Pennsylvania fluvial, deltaic, and marine clays and shales from north Texas was determined by X-ray diffraction. Deltaic lithotypes are of moderate illite, subordinate kaolinite, minor vermiculite and mixed layer composition. Nonmarine (red bed, coaly shales) lithotypes range from this composition to highly (+90 per cent) kaolinitic types, and generally lack vermiculite or chlorite. The marine shales contain a clay-mineral suite which is very similar to that of deltaic beds, but usually contain poorly- to well-crystallized chlorite. These variations are interpreted as results of two opposing mechanisms of clay-mineral genesis: degradation and desilication of detrital clay-micas, and formation of kaolinite, in nonmarine milieux; and regrading of detrital vermiculite to better-crystalline chloritic minerals by magnesium adsorption in marine waters.

The study reveals three pertinent points about clay-mineral environmental relationships:

1. The potential effects of nonmarine clay-mineral alteration processes are of much greater consequence than are those in marine environments. In this case, they led to the formation of beds in which the clay-mineral suite is almost all kaolinite, whereas the gross qualitative detrital clay-mineral suite was little changed in marine waters.

2. The actual extent and effect of the clay-mineral formation processes is quite variable, so that there is considerable overlap in clay-mineral composition between nonmarine and deltaic deposits.

(3) "Trace" clay-mineral constituents may be more sensitive environmental indicators than the gross clay-mineral composition, in this case presence or absence and crystallinity of the chlorite–vermiculite component was the most diagnostic parameter.

INTRODUCTION

A STUDY was made of clay-mineralogical variations in Cisco (U. Penn.) fluvial, deltaic and marine clays and shales of north-central Texas. This work is part of a broad-scale investigation of upper Paleozoic clay and shale mineralogy in this area (Shover, 1961).

The mineralogy, particularly the clay mineralogy, of the upper Paleozoic

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clay rocks of this area bears the imprint of a complex set of geologic factors. These include provenance, diagenetic alteration of detrital sediment, and "extrabasinal" volcanic influences. The Cisco beds show significant variations in clay-mineral composition which are apparently related to different types and degrees of alteration of the detrital clay-mineral suite in a wide variety of depositional environments.

GEOLOGIC BACKGROUND

In late Paleozoic time north-central Texas was the site of a shallow-water depositional basin which lay west of the Ouachita orogenic belt, south of the Amarillo–Wichita–Arbuckle uplift, and east of the Texas Peninsula or Concho Arch foreland (Fig. 1). During late Pennyslvanian time Ouachita-derived fluvial, paludal, lacustrine, deltaic, and shallow marine deposits, now called the Cisco beds, were deposited in the area.

It should be briefly noted that the term "Cisco" as used here differs slightly from current stratigraphic usage. Plummer and Moore (1921) classed the Graham, Thrifty, and Harpersville formations as the "Cisco group", a lithostratigraphic unit. Later workers, seeking to better correlate the Cisco of Texas with the Midcontinent Pennsylvanian section, gradually changed it into a time-stratigraphic unit equivalent to the Virgilian series. They lowered the upper boundary of the Cisco "series" on paleontological bases as part of this change (Cheney, 1940). Thus the uppermost Harpersville beds of the old "Cisco group" are now classed as lowermost Permian, Wolfcampian series. The writer found that, in the regional context, the old "Cisco group" constitutes a discrete clay-mineral stratigraphic unit, and prefers to use that term here, rather than "uppermost Cisco-lowermost Wolfcampian," for convenience.

The general outlines of Cisco stratigraphy and sedimentation are fairly simple. The series is thickest (approximately 1000 ft) in Jack and Young counties, in the northeastern part of the outcrop belt. In this area the Cisco consists of massive chert pebble conglomerates and sandstones, yellow-olive-gray mudstones, light gray claystones, and coals and coaly shales. Limestones are subordinate. Farther south and west the section thins (to 600 ft in Brown county), and is more "marine", with olive-gray and blue-gray shales and thin marine limestones predominating. Red and maroon
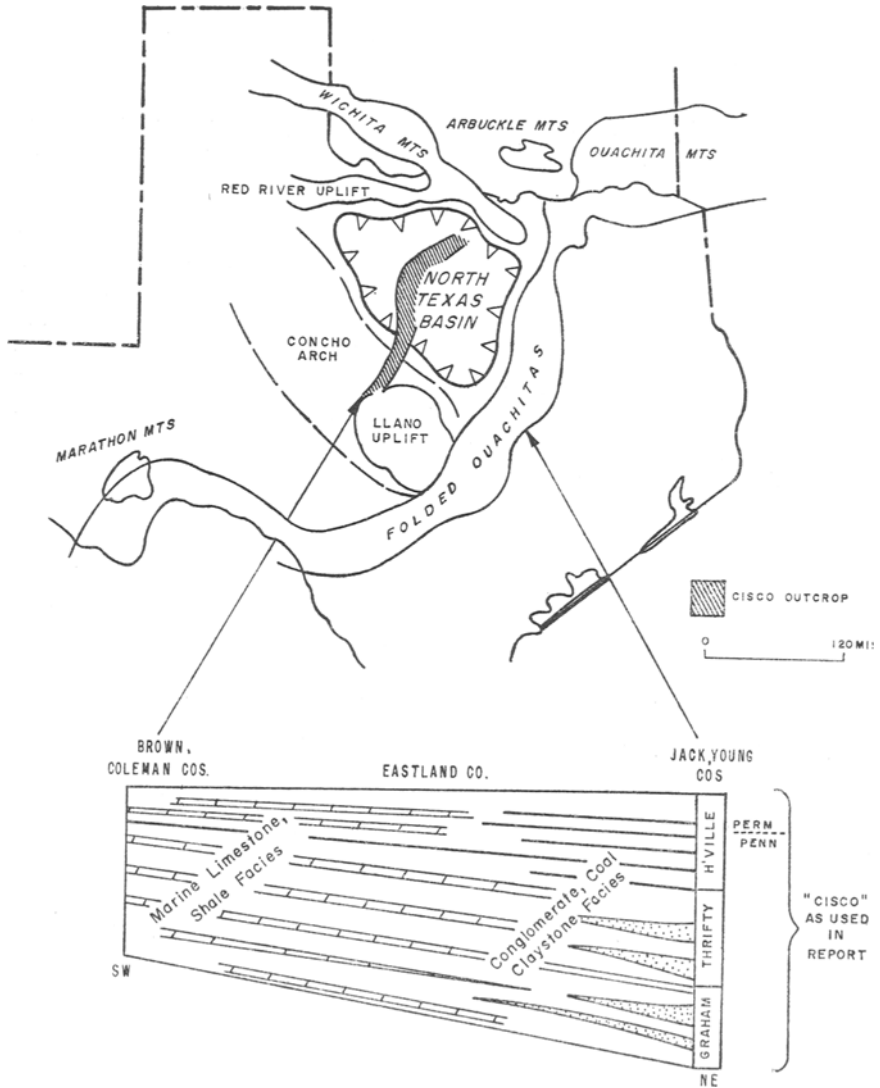
FIGURE 1.—Late Pennsylvanian paleotectonic map of Texas and schematic Cisco stratigraphic section.

shales, a few feet thick, are present in the southwest part of the outcrop belt.

The gross regional variations in Cisco lithology, together with provenance studies of the conglomerates (Bay, 1932), serve as the basis for a generalized paleogeographic reconstruction. The thickest deposits, fluvial–deltaic gravels, sands, peats, clays, and muds, were deposited in the northeast, near the Ouachita source area. Farther south and west, away from the land area, finer-grained "subaqueous deltaic" and marine clays and lime muds were the more common sediments.

This simple reconstruction is very generalized, because there is evidence for considerable shifts in facies boundaries during Cisco time. Thin limestones are found within the conglomerate-coal-clay facies of the northeastern outcrops; to the southwest, a coal bed was once mined in Coleman county. Many small-scale lateral lithologic variations exist, and pinchouts and facies change are common. Many minor unconformities and channels have been found. The study of the lithologic complexities of the Cisco section is still in its beginning stages (Nickell, 1938; Brown, 1960). However, the regional geologic and paleogeographic picture outlined above can serve as an adequate background for discussion of general trends in clay-mineral composition.

ANALYTICAL METHODS

The mineralogical composition of 149 Cisco samples was determined by X-ray diffraction analysis. About 50 grams of sample were dispersed in distilled water with 0.1 N NH_4OH. Oriented aggregates of the $< 62\mu$ and $< 2\mu$ fractions were prepared on glass slides. The samples were analyzed by X-ray diffraction, using a GE XRD–3 unit with Cu–Kα radiation. The $< 62\mu$ sample was run in the air-dried state; $< 2\mu$ slides were run (1) in the air-dried state, (2) after heating to 550°C for 1 hr and (3) after 24 hr exposure to ethylene glycol fumes.

Heavy mineral, differential thermal analysis, and thin section data were obtained as part of the larger study of which this paper constitutes a part. X-ray mineralogical data will be emphasized, however, since they provide the bulk of the information used in the study.

QUALITATIVE AND SEMIQUANTITATIVE EVALUATION OF X-RAY DATA

The qualitative mineralogical composition of the Cisco clays and shales is fairly uniform. Quartz, kaolinite, illite, and a mixed layer of illite–vermiculite mineral are present in all samples. Calcite, probably shell matter, is present in many of the deltaic and marine shales. Feldspar was not found

in the samples analyzed. A 14Å "chlorite–vermiculite" mineral is present in approximately half of the samples. This component can be further defined on the basis of the effects of heating to 550°C on the 14Å peak. "Vermiculite" collapses to 10Å upon heating, "poorly crystallized chlorite" partly collapses to about 12.5Å, "well-crystallized chlorite" is not collapsed, as the 14Å peak is unaffected by heating.

The most significant gross mineralogical parameters are variations in the relative abundance of the kaolinite, "clay mica" (illite plus chlorite–vermiculite), and mixed layer clay-mineral components. To determine these variations, a method of semiquantitative clay-mineral estimation was devised, which was patterned after earlier work in this field (Schultz, 1953). X-ray peak shapes and sharpness are sufficiently characteristic for each of the several components encountered in this study to permit
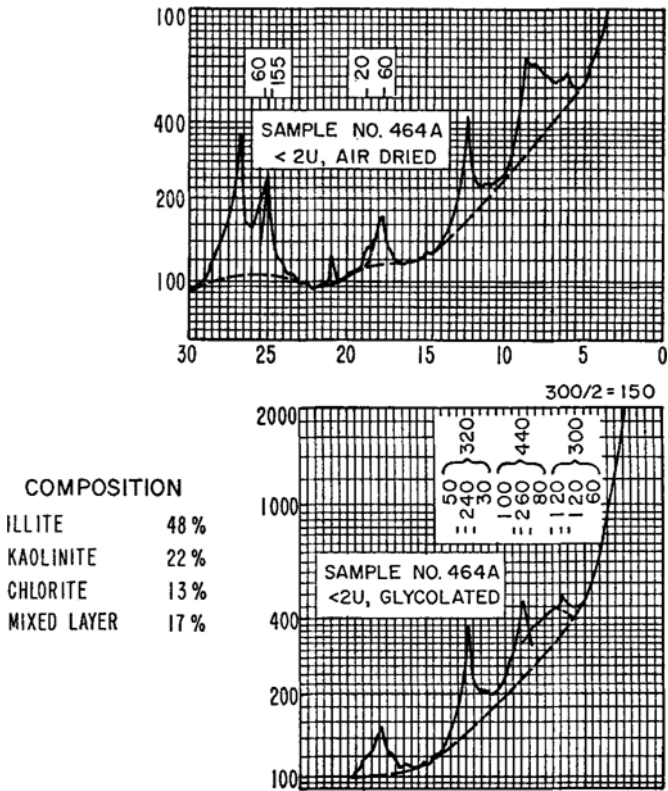

FIGURE 2.—Example of quantitative mineralogical determination by X-ray diffraction.

its application here. The method would not necessarily be applicable to all clay sediments.

The steps in the writer's method of semiquantitative clay-mineral determination are as follows. Figure 2 will serve as an illustration of the procedure.

1. The "areas" of the 12–13Å (mixed layer), 10Å (illite), and 7Å (kaolinite + chlorite) peaks in patterns for glycolated $< 2\mu$ samples were first determined. This was done by summing up peak intensity (in chart units) at peak maximum and $\pm 0.5°2\theta$.

2. The "area" of the 12–13Å mixed layer peak was divided by 2 to roughly correct for low-angle polarization. In the case of samples from other north Texas formations which contain montmorillonite (none found in the Cisco), the area under the 17Å peak was divided by four, as a rough scattering correction.

3. The areas of the three peaks were added. Each peak area was then recalculated on a 100 per cent basis. This was taken to give the relative abundance of mixed layer, illite, and kaolinite + chlorite clay minerals.

4. The 7Å component was then apportioned between kaolinite and chlorite components. In these samples the kaolinite (002)—chlorite (004) doublet at around $25°2\theta$ could usually be resolved. The intensity of the chlorite (004) peak at $25.2°\theta$ (3.53Å) "perched" on the kaolinite (002) peak at $24.9°\theta$ (3.57Å) was compared with that of the latter peak, to give a rough idea of the relative amount of kaolinite and chlorite in the total 7Å component. An additional check was provided by comparison of the intensity of the chlorite (003) peak at $18.8°2\theta$ (4.7Å) with that of the illite (002) peak at $17.8°2\theta$ (5A). This kaolinite–chlorite evaluation is the weakest part of the semiquantitative estimation procedure, but the writer feels it is sufficiently accurate for determining whether kaolinite constitutes, for instance, one-third, one-half, or one-quarter of the total 7Å component.

5. The clay-mineral composition of each sample was then tabulated in terms of relative abundance of illite, kaolinite, mixed-layer clay-mineral and chlorite–vermiculite (defined in terms of crystallinity on basis of response to heat treatment as discussed above).

The method chosen to graphically represent the clay mineral composition of samples was to construct sample density contour maps on triangle diagrams (Figs. 3 and 4). Samples were plotted on triangles in which the end members are "clay-mica" (illite plus chlorite–vermiculite), kaolinite, and mixed-layer clay mineral. The triangles are divided into 100 smaller triangles by the intersection of the ten-percentile tickmarks along the sides. The number of sample points falling within each of these small triangles was counted. This number was plotted beside a point at the center of the small triangle. After completing this, the numbers were contoured to produce a "three-dimensional histogram" of the three clay-mineral components. Histograms of illite content and chlorite–vermiculite type were also prepared for each sample category.
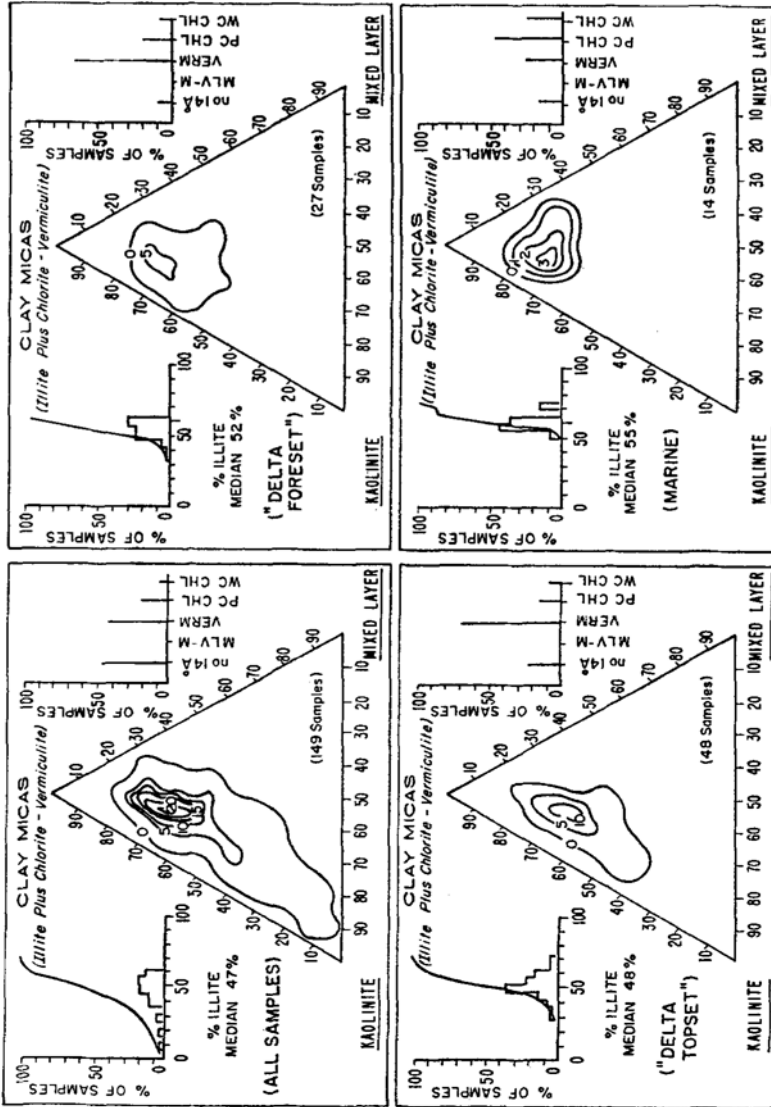
Figure 3.—Cisco clay mineralogy: all samples, and deltaic-to-marine lithotypes.
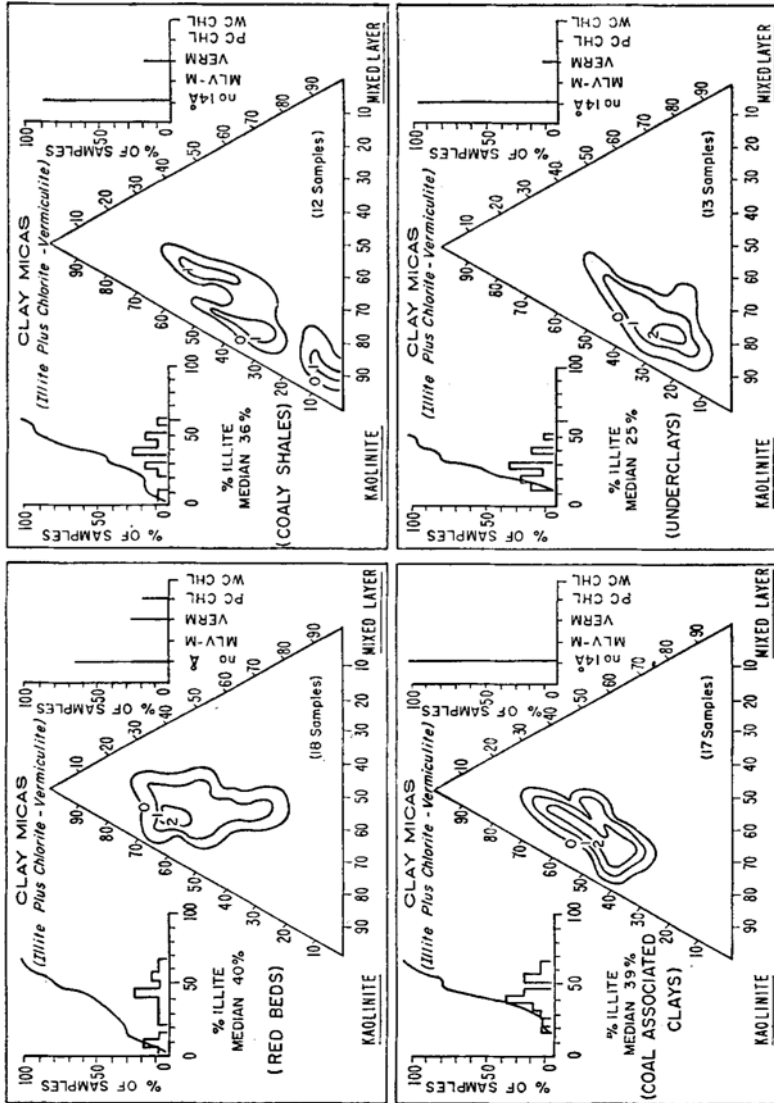
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FIGURE 4.—Cisco clay mineralogy: non-marine lithotypes.

CISCO CLAY MINERALOGY: DESCRIPTIVE

The triangle diagram for all samples analyzed (in Fig. 3) reveals a wide range in clay-mineral composition. The bulk of the samples, shown by the "crest" of the contour diagram, has a composition of about 60 per cent clay micas, 25 per cent kaolinite, and 15 per cent mixed layer clay mineral. Modal illite content is 50–55 per cent. All types of chlorite–vermiculite are found; almost half the samples have no 14Å component. But this diagram is "skewed" towards the kaolinite end of the triangle and some samples contain a clay-mineral suite composed of as much as 90 per cent kaolinite.

The clay mineralogical variations are most impressive when plotted separately for several lithologic categories which are interpreted as suggestive of different depositional environments. These categories are as follows:

1. "Delta topset" beds—yellow, olive-gray, gray, blocky mudstones with sparsely disseminated carbonaceous debris. These are commonly associated with conglomerates and coals and are interpreted to be indicative of a subaerial delta plain environment of deposition, by analogy to the criteria developed by Scruton (1960) for Mississippi delta sediments.

2. "Delta foreset" beds—olive-gray, sometimes laminated, shales. These are thought to be deposits of the subaqueous delta plain and slope, again by analogy with Scruton's work (1960).

3. Marine shales and claystones. Dense, homogeneous, gray-blue, gray claystones, of the sort found typical of the delta "bottom-set" facies by Scruton (1960), were interpreted as marine. Gray-blue and gray shales, which often contain marine fossils, were also classed as marine beds.

4. Red beds—the relatively thin red and maroon shales of the southwestern part of the Cisco outcrop belt were considered as nonmarine, probably oxidized and leached flood plain material.

5. Coaly shales—these were considered nonmarine, paludal deposits.

6. "Coal-associated clays"—fine-grained, massive gray units 5–10 ft thick, overlain or underlain by coals (excluding underclays) were also considered nonmarine, probably lacustrine, deposits.

The clay mineral composition of the six lithologic types defined above is presented in the series of triangle diagrams, Figs. 3 and 4. The "delta topset" mudstones contain a "modal" Cisco clay mineral suite of 60 per cent clay-mica, 25–30 per cent kaolinite, and 20–25 per cent mixed layer clay. Modal illite content is 50–55 per cent. Most (70 per cent) of the 48 samples of this type contain vermiculite.

The "delta foreset" samples are mineralogically similar to the "topset"— 65 per cent clay-mica (modal illite 55–60 per cent), 25 per cent kaolinite and 15 per cent mixed layer clay. As in the "delta topset" samples, vermiculite is the predominant 14Å mineral.

The Cisco "marine" shales are very similar in gross clay mineralogy

to the "delta foreset" types: 65 per cent clay-mica (55–60 per cent modal illite), 20 per cent kaolinite, and 15 per cent mixed layer clay. However, most (70 per cent) of the samples contain a poorly to well-crystallized chlorite mineral, rather than vermiculite.

The nonmarine lithotypes are considerably more variable in clay-mineral composition than the deltaic-to-marine types. As a group, they tend to contain more kaolinite, and less well-crystallized chloritic material, than the latter. The red beds, for instance, have a "modal" composition of 60 per cent clay-mica, 30 per cent kaolinite, and 10 per cent mixed layer clay; most (60 per cent) contain no chlorite–vermiculite mineral. But some contain as much as 50 per cent kaolinite and 25 per cent clay-mica and 25 per cent mixed layer clays.

The coaly shales vary from about 55 per cent clay-mica, 30 per cent kaolinite, and 15 per cent mixed layer clay to > 90 per cent kaolinite. Most (85 per cent) contain no chlorite or vermiculite. The "coal-asso-ciated" clays vary less, from about 65 per cent clay-mica and 25 per cent kaolinite to 35 per cent clay-mica and 60 per cent kaolinite. None of the samples of this clay type which were analyzed contain any chlorite–vermiculite mineral.

INTERPRETATION OF CISCO CLAY MINERALOGY

The relationship between clay mineralogy and lithology can be ex-plained in terms of fairly well accepted concepts of clay-mineral alteration in freshwater, deltaic, and marine environments. One such concept is degradation and desilication of detrital clay-micas, and formation of kaolinite. Another is adsorption of magnesium from sea water by detrital degraded micas to produce better-crystalline chloritic minerals (Powers, 1957). Most students of clay mineralogy would agree that these processes are operative; the main difference of opinion would be in the extent to which they modify the detrital clay-mineral composition in a particular geologic case.

The geographic–stratigraphic clay-mineral distribution patterns in north Texas upper Paleozoic clays and shales suggest that the gross "moderate illite, subordinate kaolinite" suite of the deltaic lithotypes is representative of the detrital clay–mineral suite carried into this area during Cisco time. It is interpreted as a second-cycle clay-mineral suite, composed of re-eroded older Pennsylvanian illite–chlorite–kaolinite bearing shales, plus Cisco-age kaolinite and mixed layer clay weathering products (Shover, 1961).

Upon deposition in the Cisco basin, this detrital clay-mineral suite underwent varying degrees of change along two opposed "paths of altera-tion" (Fig. 5). Sediment deposited in fluvial, paludal, and lacustrine milieux was subjected to degradation and desilication of detrital clay-

micas, and formation of kaolinite. This effect could be the result of alteration *in situ*; or reworking and redeposition of weathered flood plain material could form highly kaolinitic deposits. Precipitation of colloidal desilication products could also account for some of these beds. Without detailed field
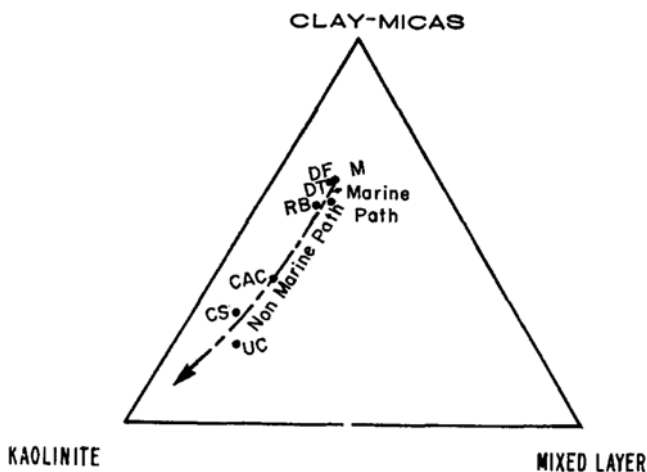

FIGURE 5.—"Paths of alteration" suggested by clay mineralogy of Cisco clays and shales.

information and petrographic data for such clays, the precise mode and operation of this process cannot be deduced in a given case. It obviously varied greatly in extent; in some cases, the only effect was destruction of detrital vermiculite; in other cases, almost complete alteration to kaolinite ensued. This explanation of the nonmarine clay mineralogy is supported by the broad, "shaggy" diffraction peaks produced by the illite in the more kaolinitic beds, which are suggestive of leaching and degradation.

Comparison of clay mineralogy of "known" nonmarine beds and underclays also offers a clue as to the origin of these deposits. Cisco underclays show the same range in clay mineralogy as the nonmarine lithotypes described above (Fig. 4). "Modal" clay-mineral content is 70 per cent kaolinite, 20 per cent clay-mica, and 10 per cent mixed layer clay mineral. Most (97 per cent) contain no vermiculite or chlorite. This can be logically interpreted to mean that these underclays, like many in the Midcontinent and Illinois Basin, are the result of nonmarine desilication of clay-micas and formation of kaolinite. Without detailed study of a particular deposit, of course, one could not say whether it is a paleosol, product of "subaqueous

weathering" (a "gley"), or a result of precipitation of colloidal silica and alumina to form kaolin.

The other path of alteration, in the marine environment, was much more restricted. In the samples analyzed, the only detectable change was the alteration of detrital vermiculite to a poorly-to-well-crystallized chlorite by adsorption of magnesium from sea water. In this case, at least, the "ideal" marine clay-mineral suite of illite and chlorite apparently did not form by diagenetic alteration.

CONCLUSIONS

Differences in clay-mineral composition among Cisco clays and shales can be interpreted in terms of what are by now fairly well-accepted concepts of marine and nonmarine clay-mineral genesis. These concepts, (1) destruction of micas and formation of kaolinite in nonmarine milieux and (2) regrading of detrital degraded micas in marine waters, are not new. But three very important aspects of their operation are apparent in this case. These may be of interest to those seeking a more balanced view of clay-mineral environmental relationships than theoretical mineral-stability considerations would afford. These are:

1. The ultimate extent of the nonmarine clay-mineral alteration processes is much greater than the marine processes in Cisco sediments. Some nonmarine beds are almost wholly kaolinite, whereas the marine types have the same gross clay-mineral composition as the deltaic types.

2. Both nonmarine and marine alteration vary in effect, and there is considerable overlap in clay-mineral composition between rocks of different environments. The red beds, for instance, show a wide range in clay-mineral composition, from a suite which is indistinguishable from deltaic types, to almost wholly kaolinite beds. The evidence for the operation of these processes in this case is of an inferential, statistical nature.

3. Very minor, subtle clay mineralogical variations may be more reliable and consistent indicators of diagenetic change than gross clay mineralogical parameters. In this case, the presence or absence, and crystallinity, of the chloritic component appears to be a more diagnostic index of depositional environment than the quantitative clay-mineral composition.

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