MASON G SPACKMAN LK 00/00/1984 PAGE 1 OF 1

MINERALOGIC CHARACTERIZATION OF A CHATTANOOGA SHALE CORE FROM CENTRAL TENNESSEE

Reference #

Data Inventory Sheet

1. Commodity OS

2. Author Mason, G.

Mineralogic Characterization of a Chattanooga Shale Core from Central – Tennessee: Mason, G. M., Spackman, L. K., Leimer, H. W.; Eastern Oil Shale Symposium Proceedings, Lexington, KY, ^November 26-28 1984. pp. 393 – 400

4. Date

5. Reference

6. Source
in house

7. Location of Data
Author file

8. Form of Data

9. Type of Work

10. Description of Work

11. Types of Data

12. Quantity of Data

13. Quality of Data

14. Priority

Ref OK

Mineralogic Characterization of a Chattanooga Shale Core from Central Tennessee

by

Glenn M. Mason and Lowell K. Spackman
Western Research Institute
P.O. Box 3395, University Station
Laramie, Wyoming 82071

H. Wayne Leimer
Department of Earth Sciences
Tennessee Technical University
Cookeville, Tennessee 38501

Abstract

The Chattanooga Shale was deposited over much of present Tennessee when Devonian seas transgressed, leaving a thick deposit of organic rich black mud. The Chattanooga Shale ranges in thickness from less than 35 feet in central Tennessee to more than 720 feet in the eastern portion of the state. Although much thinner, the central Tennessee section of the shale appears much richer in extractable organic material, averaging 13% carbon (approximately 9.3 gallons per ton by Fischer assay) with a maximum of 20% carbon (15 gallons per ton). In central Tennessee, the Chattanooga Shale has two members, the Dowelltown and the Gassaway and is underlain by the Leipers Limestone and overlain by the Ft. Payne Chert and Maury Formation, a phosphatic claystone. Detailed mineralogy from a corehole taken in DeKalb County, as determined by X-ray diffraction, indicates a mineral assemblage composed primarily of quartz (59%), feldspars (14% predominately K-feldspar), pyrite (8%), and clay minerals (19%). The clay mineral assemblage was composed of illite, mixed layer illite-smectite, kaolinite, and chlorite. The noted abundance of kaolinite (5 to 29% of total clay fraction) differs significantly from data of other investigators, possibly suggesting a proximity to an ancient shoreline. Additionally, the samples from this corehole were higher in quartz and feldspars, and lower in overall clay mineral percentages than samples of the Chattanooga Shale reported in other areas.

Introduction and General Geology

When late Devonian seas advanced across the central North American continent some 340 million years ago, conditions were different than when other invasions occurred. The environment that resulted was like few others in all the geologic history of the region. This Devonian sea eventually spread over much of the present eastern United States, depositing a black, carbonaceous mud over hundreds of thousands of square miles. This black mud, containing rotted organic matter, became known as Antrim Shale in Michigan, Ohio Shale in Ohio and northeastern Kentucky, New Albany Shale in northwestern Kentucky and Indiana, and Chattanooga Shale in southern Kentucky, northern Alabama and throughout Tennessee (Conant and Swanson, 1961).

At the time of its deposition, the Chattanooga Shale was widely distributed, covering nearly all of Tennessee except for two areas: one near Hohenwald (Lewis County) and the other near Ashland City

1984 Eastern Oil Shale Symposium • *November 26-28, 1984* • *University of Kentucky Institute for Mining and Minerals Research and the Kentucky Energy Cabinet.*

(Cheatham County). Erosion has removed the shale from west Tennessee, most of the Central Basin, and most of the Valley and Ridge Province. Folding and faulting further obscure its distribution in the Valley and Ridge Province (Hickman and Lynch, 1967).

The Chattanooga Shale is overlain by the Fort Payne Chert and the Maury Formation, which is phosphatic immediately above the Chattanooga contact and is unconformably underlain by the Leipers Limestone. The formation is subdivided into two members: the upper consists of the Gassaway Member (subdivided into upper, middle, and lower) and the lower is called the Dowelltown Member (subdivided into upper and lower). A good marker is the Center Hill Ash Bed, which occurs in the upper Dowelltown approximately 0.8 to 1.5 feet below the Gassaway-Dowelltown contact. This bed is difficult to distinguish in outcrop and cores, and in many localities is throughly mixed with the surrounding shale.

General mineralogy of the Chattanooga Shale consists primarily of quartz, clay minerals, feldspar (mostly K-spar), pyrite, calcite, and others. Additionally, the shale is composed of approximately 5-20% organic matter.

Figure 1 portrays the generalized area of Tennessee underlain by Chattanooga Shale. Samples for this study were obtained from a corehole drilled in DeKalb County, Tennessee.

Samples from the core were selected on the basis of observed lithologic changes at approximately one-foot intervals. Mineralogy of all samples was determined by X-ray diffraction (XRD) utilizing a Philips APD 3600 automated diffractometer system. The XRD system was operated at 45 KV, 40 mA using $CuK\alpha$ radiation, filtered by a diffracted-beam graphite monochronometer with theta-compensating slit. Identifications were made utilizing computer assisted search-match software supplied by Philips. Material balances reported were generated by the software using a least-squares method on a percent volume ±100% basis.

Mineralogic character of all samples was determined for both bulk mineralogy and clay minerals separation. A complete discussion of the procedures used for the preparation of bulk mineralogical samples is available in Mason (1982) and Mason et al. (1984).

Sample preparation and X-ray procedure for the clay mineral fraction consisted of the following: 1) placing three grams raw shale in a large beaker, heating with 30% H_2O_2 to extract organic matter as described in Jackson (1974); 2) dispersing clay minerals in distilled water with ultrasonic disaggregation and sodium metaphosphate (calgon) when needed; and 3) performing gravimetric separation of the clay minerals to isolate the two micron (μ) and smaller particles. After the clay fraction was isolated, samples were prepared using KCl and $MgCl_2$ solutions. K-saturated samples were heated to 550°C to observe possible peak collapse; Mg-saturated samples were solvated with ethylene glycol to observe peak shifts associated with expanding clay minerals. All clay samples were mounted on glass slides using the millipore peel method as described by Drever (1973). Raw samples and Mg-saturated samples were scanned 2 to 60° 2θ, while Mg-saturated glycolated, K-saturated, and K-saturated-heated samples were scanned 2 to 22° 2θ.

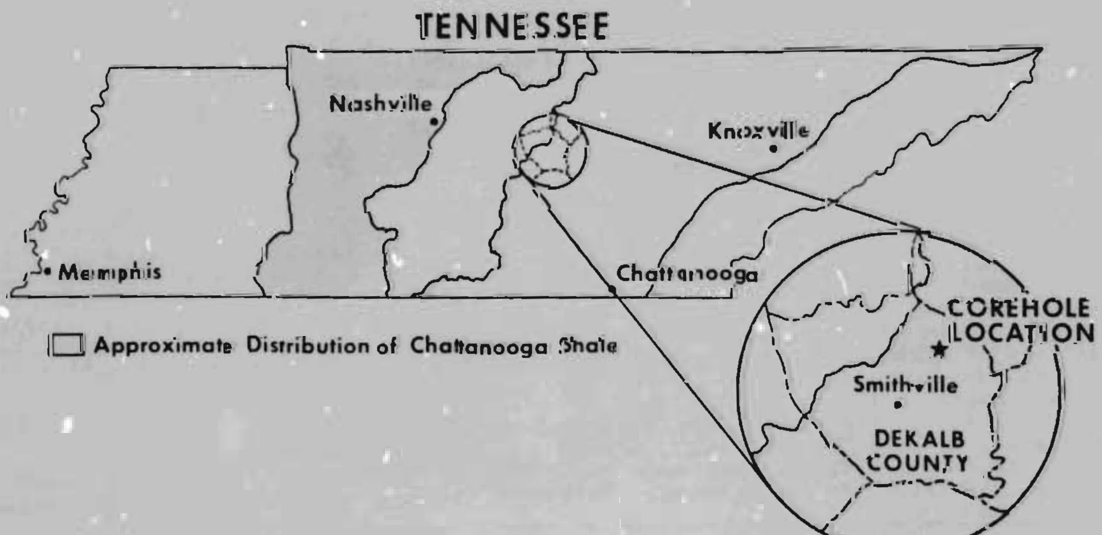

Figure 1. Location of study area showing approximate outline of Chattanooga Shale distribution in Tennessee.

Modified Fischer assay analyses (Stanfield and Frost, 1949) were performed on each sampled interval. Fischer assay was developed for Green River Formation oil shales, and its validity for predicting oil yield from the leaner eastern oil shales is somewhat questionable because of the differences in the kerogenaceous material. However, standardization of the Fischer assay analysis allows information for geologic (i.e. stratigraphic) correlations to be obtained (Figure 2).

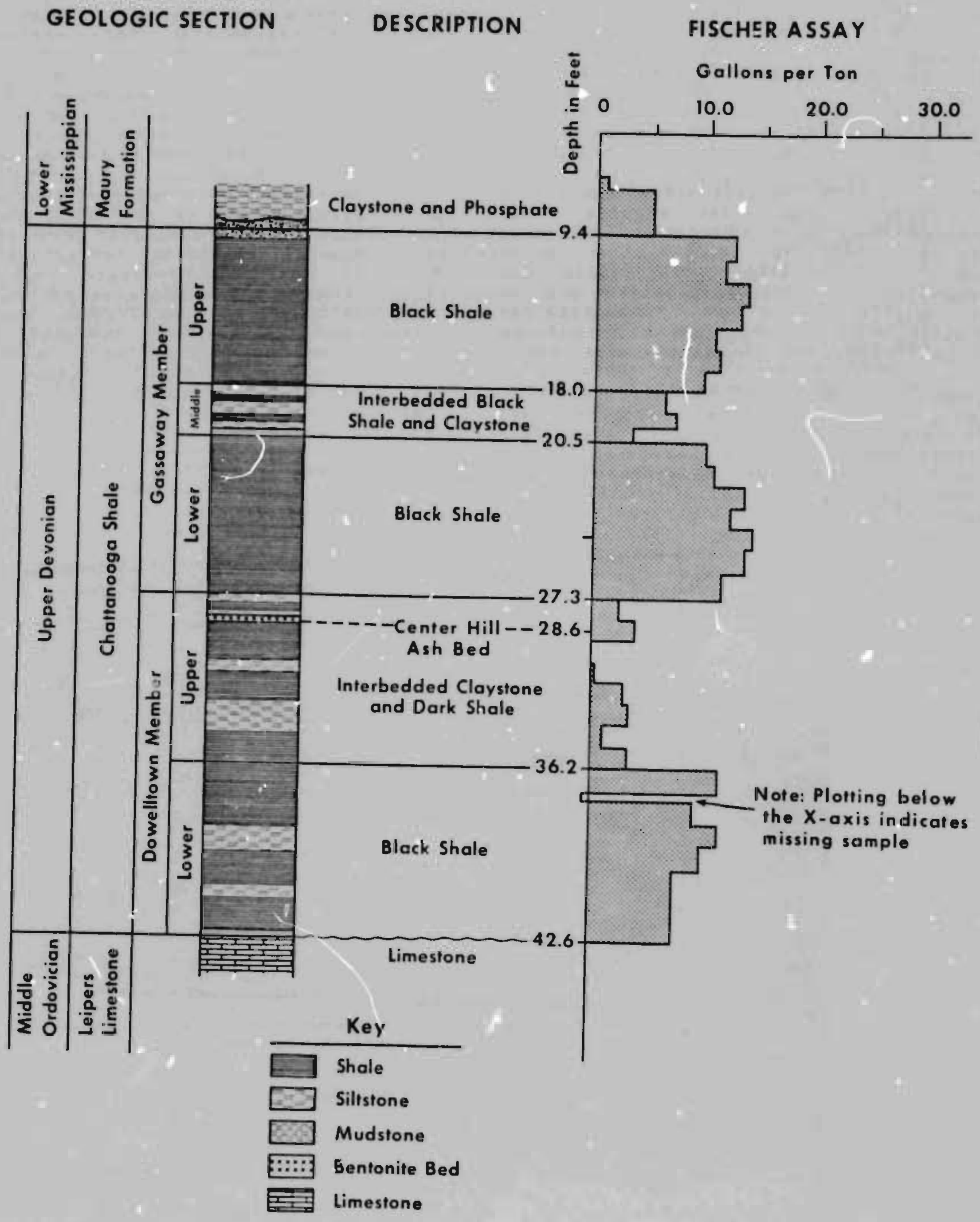

Figure 2. Geologic section, description, and Fischer Assay correlation for Chattanooga Shale in study corehole.

Results

Bulk Minerals

Bulk shale mineral results are graphically displayed in Figure 3. The Chattanooga Shale in this corehole was 33.2 feet in thickness, ranging from 9.4 to 42.6 feet in depth from the surface. Primary minerals reported in the raw shale were quartz (avg. 59.0%), clay minerals (avg. 16.0%), feldspars (avg. 14.0%), pyrite (avg. 8.0%), and the remaining percentage was composed of dolomite, calcite, sphalerite, siderite, and apatite, all of which had irregular occurrences and abundances.

From the bulk mineralogy, the stratigraphic boundaries of the Chattanooga Shale could be observed. The contact with the underlying Leipers Limestone could be distinctly determined as it is unconformable and involves an extreme mineralogical change from carbonate rocks into the overlying shale. An interesting note was that the two feet of Leipers Limestone samples X-rayed were actually composed predominately of dolomite (approx. 85%). The Maury Formation, which overlies the shale, could also be easily determined because of the abundant occurrence of the phosphate mineral apatite (17-18%).

Within the Chattanooga Shale itself, bulk mineralogical changes were more difficult to distinguish. Pyrite abundances generally increased as organic content increased; however, the correlation was not strong because pyrite was moderately abundant and well dispersed throughout the entire section. Feldspars decreased in abundance at the top and bottom of the shale section due to changes in the depositional environment. Generally, potassium feldspar was observed to be three to four times more abundant than sodium feldspar, except in the Upper Dowelltown in which the abundances were approximately equal. This change in the ratio of sodium to potassium feldspar correlated very strongly to a decrease of organic matter in the Upper Dowelltown, possibly indicating a slightly different environment during its deposition. Calcite occurred as random carbonate stringers in the shale and displayed no distinctive pairing with other minerals.

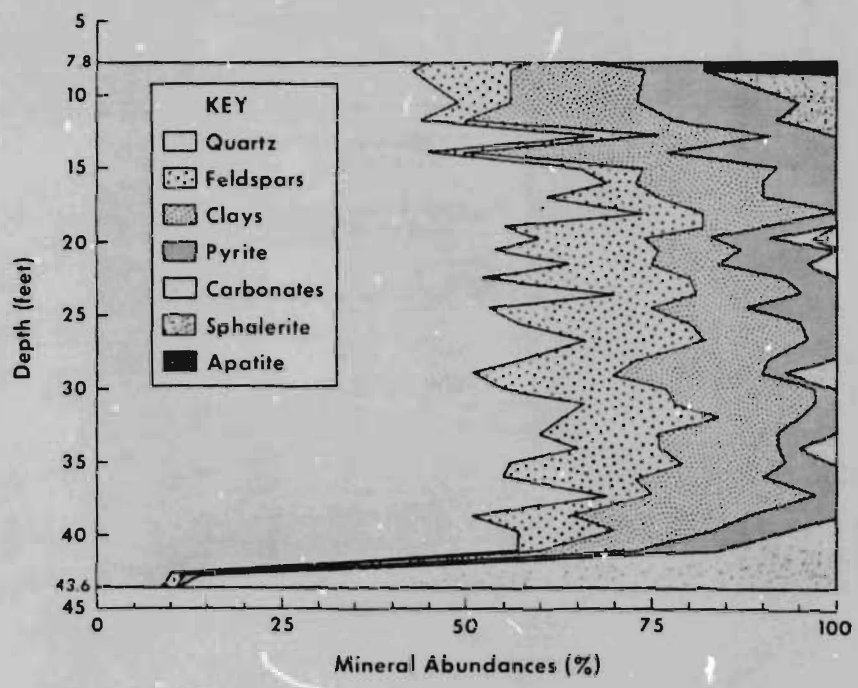

Figure 3. Bulk mineral identification of Chattanooga Shale.

Clay Minerals

Clay minerals are graphically displayed in Figure 4. Four clay minerals were identified from this corehole. The most abundant clay mineral was illite, composing an average of 51% of the total clay fraction; the next most abundant were mixed-layer clays comprising an average of 30%; then kaolinite averaging 11%, and least abundant was chlorite averaging 8%.

Illite in this report was considered to be 2M muscovite, $KAl_2(Si_3Al)O_{10}(OH)_2$. Illite is recognized on X-ray diffraction traces by its strong first-order (001) peak at 10A, a weak second-order peak at 5A, and a third-order (003) peak at 3.3A. Material that did not expand at 10A when treated with ethylene glycol or collapsed when heated was considered illite.

Mixed-layer clays represent a high level of difficulty in identification. Mixed-layer clay minerals can be a random or regular interlayering of two or more clay minerals. Mixed-layer clays identified in this study were believed to be predominantly a random illite-smectite, but because of the complexity of the samples and determinative capabilities of X-ray diffraction techniques, some proportion of the mixed-layer clay could have been an illite-chlorite as suggested by Hosterman and Whitlow (1983). However, no positive verification of the illite-chlorite mixed-layer clay could be determined from the samples studied. The illite-smectite mixed-layer clay was considered a random interstratification because of the intermediate location of its peak between 10A and 14A. Random mixed-layer clays produce intermediate peaks while regular mixed-layer clays produce additive peaks. The mixed-layer clays were identified and quantified by comparing the 10A peak and examining the shift as a result of glycolation and peak collapse as a result of heating. The intermediate peak expected for a random illite-smectite mixed-layer was obscured by the 10A peak, making accurate identification difficult. Because of the abundant illite at 10A and the mixed-layer also appearing near this same peak, it is plausible that the mixed-layer clay was of the 80/20 illite-smectite type reported by Weaver and Wampler (1970). Expendable clays collapse upon heating. Therefore, the amount of mixed-layer clay was calculated by the difference in area of the K-saturated versus K-saturated-heated sample. The amount of peak collapse at the 10A position was considered to be the mixed-layer illite-smectite.

Kaolinite ($Al_2Si_2O_5(OH)_4$) was identified by characteristic 14A, 10A , and 3.5A peaks (line 1, Figure 5), with the 7A peak collapsing completely upon heating in the K-saturated sample (line 2, Figure 5). Material at the 14A position remaining after heating was considered chlorite, $(Mg,Fe,Al_6)(Si,Al)_4O_{10}(OH)_8$. Figure 5 is an idealized representation of X-ray diffractograms displaying the identification process used for the clay species.

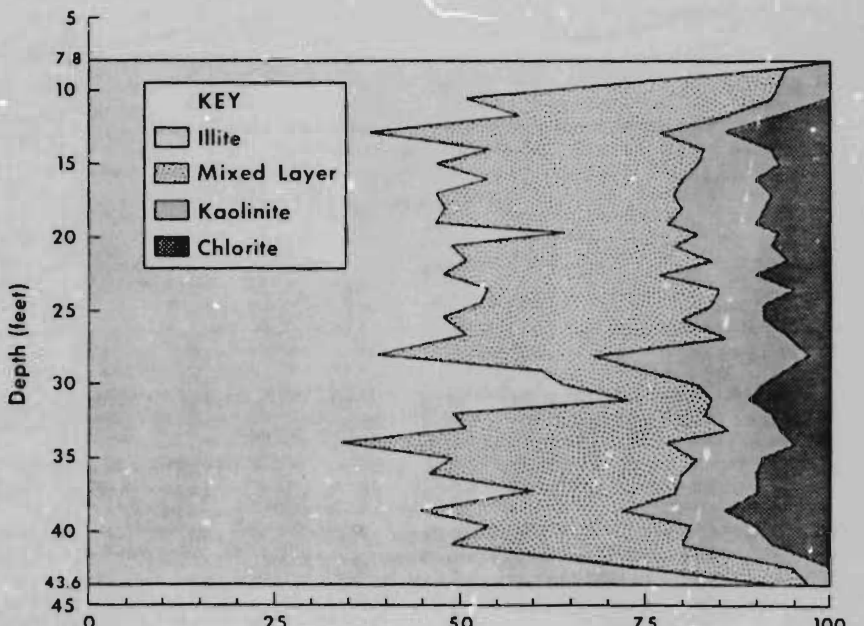

Figure 4. Clay mineral identification of Chattanooga Shale.

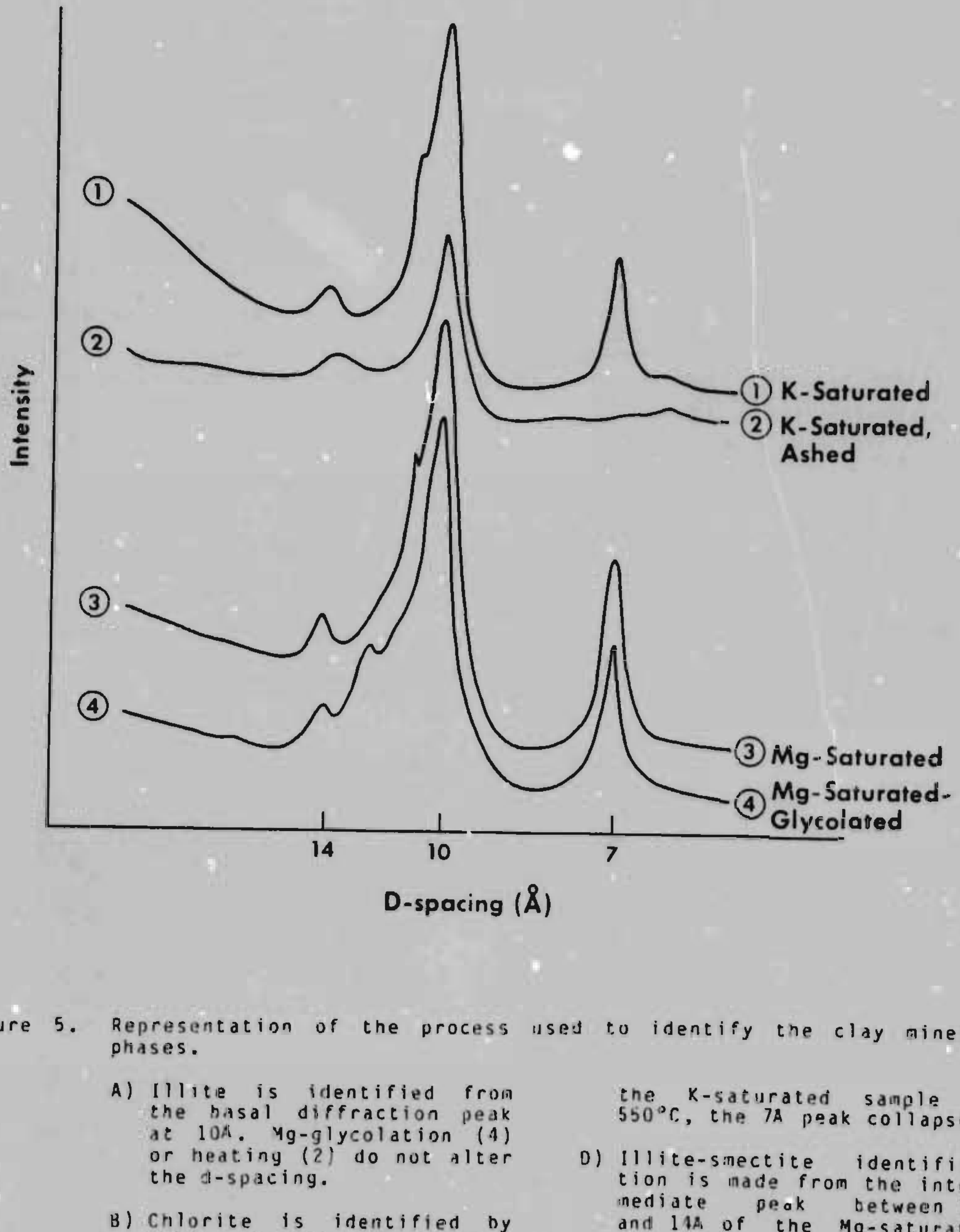

Figure 5. Representation of the process used to identify the clay mineral phases.

A) Illite is identified from the basal diffraction peak at 10Å. Mg-glycolation (4) or heating (2) do not alter the d-spacing.

B) Chlorite is identified by 14Åand 7Å peaks.Upon heating (2) and Mg-glycolation (4), no change is observed.

C) Kaolinite is identified by the 7Å peak. Upon heating the K-saturated sample to 550°C, the 7Å peak collapses.

D) Illite-smectite identification is made from the intermediate peak between 10Å and 14Å of the Mg-saturated sample. On K-saturation (1) and heating (2), the peak collapses to 10Å. Glycolation increases the peak to 12 or 13Å (4).

The pairing of clay mineral factors revealed several recognizable trends. The most obvious was the increase in kaolinite in the portion of the section containing the Center Hill Ash Bed. Even though the ash bed was difficult to distinguish visually because of mixing with the shale, a pronounced increase in kaolinite was observed from the clay mineral separation (Figure 4).

Illite and illite-smectite mixed-layer clays displayed a correlation with organic matter although not extremely well defined. In zones of the most abundant organic matter, Upper and Lower Gassaway Members and Lower Dowelltown Member, the abundance of illite-smectite increased slightly at the expense of illite. Kaolinite and chlorite displayed no pairing for organic material, but rather remained relatively constant.

Distinct clay mineral changes were observed at both the upper and lower contacts of the Chattanooga. In both cases, illite became the only clay mineral identified, even though clays still remained moderately abundant extending into the Maury Formation. Clay minerals decreased dramatically in the underlying carbonate unit as would be expected.

Discussion

Interpretation of the mineralogical data produces some interesting implications about the depositional environment during Chattanooga time at this locality. The relative percentage of quartz and feldspars (Na and K) were higher and clays lower than generally reported by other workers (Conant and Swanson, 1961; Hosterman and Whitlow, 1983). Although it is possible that some of this discrepancy could have resulted from the software analysis techniques used, the bulk mineral analysis showed excellent consistency and reproducibility. Care was taken to evaluate and separate abundances of quartz and illite because both minerals share a strong 3.3A peak. Because of this fact, illite abundances were evaluated on the basis of their 10A peak, while quartz abundances were evaluated on the ratio of the 4.2A and 3.3A peaks. All identifications were volume percent. Additionally, minerals were viewed on a compositional basis and not a particle-size basis. Differences in the usage of the terminology "clay minerals," may also account for quantitative differences. "Clay-sized" quartz accounts for a substantial proportion of the 2μ fraction.

Clay mineral components of the Chattanooga Shale probably had their origin much as described by Hosterman and Whitlow (1983). Illite was derived from degraded and disordered illite and smectite; chlorite formed from the magnesium and iron lost by the degradation of smectite; and the mixed-layer components were formed from a mixture of their single-layer components. Hower et al. (1976), attributed mineralogical and chemical variations in buried shales to the general reaction:

smectite + K-feldspar (+ mica) =
illite + quartz + chlorite.

Identification of moderately abundant kaolinite differed from findings at other localities reported in the literature (Hosterman and Whitlow, 1983; and Conant and Swanson, 1961) averaging 10% but ranging to 29% for shale containing the Center Hill Ash Bed. Volcanic ash soils are known to produce an abundance of 14A clays, predominantly smectites and kaolinite (Nagasawa, 1978). Kaolinite's relatively larger grain size introduces a physical control on distribution of the mineral (Gibbs, 1967). When transported it does not remain in suspension and is deposited closer to the source area. Kaolinite is found to be most abundant near shorelines in both ancient and modern sediments (Parham, 1966). This information, supported by the fact that quartz and feldspars composed a slightly greater volume of the samples investigated, points to consideration of a depositional environment in the proximity of an ancient shoreline. However, detecting kaolinite in sediments should not be considered unusual; Griffin et al. (1968) found kaolinite concentrations in all of modern oceanic sediments including deep sea sediments, far removed from terrestrial sources.

It is very plausible that the original source soils for the Chattanooga Shale was strongly influenced by volcanic sources (Roen and Hosterman, 1982; and Droste and Vitaliano, 1983). Evidence to support this concept would be the alteration of smectite (a principal component of volcanic soils) to illite, quartz, and chlorite.

The final answer to understanding differences in the mineralogy of the Chattanooga Shale, as well as all eastern oil shales, may lie in improved instrumentation and a better understanding of their geochemical origins. Traditionally, eastern oil shales have been characterized as having very similar mineralogies. On a macro scale they do, but on a micro scale differences in mineralogical relationships can provide valuable insights into the conditions that existed in the depositional environments and subsequent diagenetic changes the shales have undergone.

Summary

- The bulk mineralogy of Chattanooga Shale includes quartz, feldspars (predominantly K-spar), pyrite, and clay minerals, with lesser amounts of calcite, dolomite, and apatite.

- The clay mineralogy includes illite, mixed-layer clays, chlorite, and kaolinite.
- Clay minerals (hydrous alumina silicates) composed a smaller percentage of the samples than generally reported in the literature. "Clay sized" minerals, i.e. minerals of 2μ particle size, especially quartz and feldspars, were abundant.
- Kaolinite was present in all samples examined, possibly an indication of a near-shore depositional environment.
- The alteration of smectite to illite, quartz, and chlorite, plus the abundances of quartz and feldspars, could have resulted from volcanically influenced soils.
- The eastern oil shales, although similar mineralogically on a macro scale, have important differences on a micro scale that could reveal valuable information about their geochemical origins and depositional environments when more completely studied.

Acknowledgements

The authors are grateful to G. F. Dana, S. M. Dorrence, E. Esmaili, P. Marron, and R. L Oliver for their constructive comments. Additionally, the authors wish to extend their personal thanks to Jayne Adams and Jean Tweed for their patience and assistance in typing and processing this manuscript.

References

1. Conant, L. C., and Swanson, V. E., Chattanooga Shale and related rocks of central Tennessee and nearby areas: USGS Prof. Paper 357, 1961.
2. Drever, J. I., The preparation of oriented clay mineral specimens for X-ray diffraction analysis by a filter membrane peel technique: Amer. Min., v. 58, p. 553-554, 1973.
3. Droste, J. B., and Vitaliano, C. J., Tioga bentonite (middle Devonian) of Indiana: Clays and Clay Minerals, v. 21, p. 9-13, 1983.
4. Gibbs, R. J., The geochemistry of the Amazon River system: Part I. The factors that control the salinity and the composition and concentration of suspended solids: GSA Bull., v. 78, p. 1203-1232, 1967.
5. Griffin, J. J., Windom, H., and Goldberg, E. D., The distribution of clay minerals in the world ocean: Deep Sea Research, v. 15, pp. 433-459, 1968.
6. Hickman, R. C., and Lynch, V. J., Chattanooga Shale investigations: USBM Report of Investigations 6932, 1967.
7. Hosterman, J. W., and Whitlow, S. I., Clay mineralogy of Devonian shales in the Appalachian basin: USGS Prof. Paper 1298, 1983.
8. Hower, J., Eslinger, E. V., Hower, M. E., and Perry E. A., Mechanism of burial metamorphism of argillaceous sediments: mineralogical and chemical evidence: GSA Bull., v. 87, p. 725-737, 1976.
9. Jackson, M. L., Soil chemical analysis - advanced course, 2nd ed.: Dept. of Soil Science, U. of Wisconsin, 1974.
10. Mason, G. M., A technique for preparation of back loaded powder specimen for a Philips X-ray diffractometer: USDOE/LETC open file report, 5 p., 1982.
11. Mason, G. M., Williams, J. D., and Spackman, L. K., High temperature minerals in an in situ oil shale retort: Proceedings of the 17th Oil Shale Symposium, Colorado School of Mines, Golden, CO, 1984.
12. Nagasawa, K., Weathering of volcanic ash and other pyroclastic materials: in Developments of Sedimentology 26, Clays and Clay Minerals of Japan, T. Sudo and S. Shimoda, eds., Kodansha, Tokyo, Japan, 1978.
13. Roen, J. B., and Hosterman, J. W., Misuse of the term bentonite for Devonian ash bed in Appalachian basin: GSA Bull., v. 93, p. 926-928, 1982.
14. Parham, W. E., Lateral variations of clay mineral assemblages in modern and ancient sediments: in Gekker and Weiss, editors, Proceedings of the International Clay Conf., v. 1, London Pergamon Press, p. 135-145, 1966.
15. Stanfield, K. E., and Frost, I. C., Method of assaying oil shale by a modified Fischer assay retort: USBM, RI 4477, 1949.
16. Weaver, C. E., and Wampler, J. M., K, Ar, illite burial: GSA Bull., v. 81, p. 3425-3420, 1970.

END

of

PAPER