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ENVIRONMENTAL SCIENCES DIVISION

MINERALOGICAL CHARACTERIZATION OF SELECTED SHALES  
IN SUPPORT OF NUCLEAR WASTE REPOSITORY STUDIES: PROGRESS REPORT  
FOR OCTOBER 1987-SEPTEMBER 1988

S. Y. Lee, L. K. Hyder, and P. M. Baxter<sup>1</sup>

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Environmental Sciences Division  
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<sup>1</sup>Graduate student, Louisiana State University, Baton Rouge.

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## ABSTRACT

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Mineralogical characterization of selected shales in support of nuclear waste repository studies: progress report for October 1987-September 1988.  
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One objective of the Sedimentary Rock Program at the Oak Ridge National Laboratory has been to examine end-member shales to develop a data base that will aid in evaluations if shales are ever considered as a repository host rock. Five end-member shales were selected for comprehensive characterization: the Chattanooga Shale from Fentress County, Tennessee; the Pierre Shale from Gregory County, South Dakota; the Green River Formation from Garfield County, Colorado; and the Nolichucky Shale and Pumpkin Valley Shale from Roane County, Tennessee. Detailed micromorphological and mineralogical characterizations of the shales were completed by Lee et al. (1987) in ORNL/TM-10567. This report is a supplemental characterization study that was necessary because second batches of the shale samples were needed for additional studies. Selected physical, chemical, and mineralogical properties were determined for the second batches; and their properties were compared with the results from the first batches.

Physical characterization indicated that the second-batch and first-batch samples had a noticeable difference in apparent-size distributions but had similar primary-particle-size distributions. There were some differences in chemical composition between the batches, but these differences were not considered important in comparison with the differences among the end-member shales. The results of X-ray diffraction analyses showed that the second batches had mineralogical compositions very similar to the first batches, as expected from chemical analysis results. Illite was the major mineral component of the Chattanooga Shale, Nolichucky Shale, and Pumpkin Valley Shale. Dolomite was the dominant component in the Green River Formation, and smectite was the dominant component in the Pierre Shale.

Differences in the selected properties between the second and first batches were not considered important enough to warrant further characterization of the second batches of the end-member shales. The results also suggested that the compositional and physical differences were too small to influence the results of other geochemical studies, such as radionuclide sorption and rock-water interaction.

## 1. INTRODUCTION

Mineralogical characteristics of selected shales have been investigated at the Oak Ridge National Laboratory (ORNL) as a part of the Sedimentary Rock Program (SERP) in support of the U.S. Department of Energy's Repository Technology Program of the Office of Civilian Radioactive Waste Management. The purpose of SERP was to examine a variety of sedimentary rocks to determine their suitability as possible hosts for a nuclear waste repository and to transfer the scientific and technological information developed through the program to the Yucca Mountain Repository Program.

The objectives of this task were to determine the mineralogical composition and micromorphology of selected shales, to assist other SERP task groups in chemical and mineralogical interpretations of their experimental data, and to develop a quantitative mineralogical analysis method, which would be useful in identifying acceptable strata for siting a repository as well as in locating sources of repository backfill materials.

Four end-member shales were selected on the basis of their composition for comprehensive mineralogical characterization: the Chattanooga Shale was selected as representing a carbonaceous shale, the Pierre Shale as a smectitic shale, the Green River Formation as a carbonate-rich shale, and the Nolichucky Shale and Pumpkin Valley Shale as illitic shales (Stow and Croff 1987). Task activity for the first year was focused on understanding the mode of occurrence of natural uranium in the Chattanooga Shale. This study offered a unique opportunity to examine retardation rates of uranium leached from a shale-hosted repository (Lee et al. 1986). Semiquantitative mineralogical analyses of the first batch of five selected end-member shales were conducted during the second year of the activity (Lee et al. 1987). It was necessary to prepare and characterize a second-batch of samples for additional sorption and organic matter studies because the first-batch of samples were used up in earlier experiments. The core segments selected for the second-batch samples were obtained from either different sections of the same cores or from

different cores but at similar depths to the cores prepared for the first-batch samples.

The purpose of this year's progress report is to document the physical, chemical, and mineralogical characteristics of the second batch of the shale samples to allow for the proper interpretation of radionuclide sorption studies (Meyer et al. 1988). Also included in this report are the preliminary results of a clay-boiling experiment designed to examine smectite and illite stability in a dilute brine solution at elevated temperature. Because the mission of the Sedimentary Rock Program has been redirected to basic scientific and technological support for the Yucca Mountain Repository, future research activities will be focused on mineral transformations, reactivity, and microporosity relations of clay minerals from tufaceous rock.

## 2. MATERIALS AND METHODS

### 2.1 MATERIALS

Five shales, representing four end-member shale compositions, were selected for geochemical characterization studies by the Sedimentary Rock Program. The shales selected were the Chattanooga Shale, Pierre Shale, Green River Formation, Nolichucky Shale and Pumpkin Valley Shale (Lee et al. 1987). Two batches of shale samples were prepared for geochemical analyses. The first batches, collected in October 1985, were characterized in FY 1986. (The results of the study were reported in ORNL/TM-10567 by Lee et al. 1987.) The second-batch samples, obtained from different cores or different depths of same cores, were studied in FY 1987.

The Chattanooga Shale samples were from ASARCO borehole PM238, in the upper Dowelltown Member of the formation in Fentress County, Tennessee, at a depth of 141.0 to 141.5 m (first batch) and 141.5 to 142.0 m (second batch). This unit is generally described as "interbedded medium light grey claystone and dark grey shale beds" (Conant and Swanson 1961).

The Pierre Shale samples, PS/86/20U13-1T/2 (first batch) and PS/86/20U13 (second batch), were from the Mobridge Member in Gregory County, South Dakota. They were retrieved from drill hole 84-20 at a depth of 88.2 to 88.9 m. The samples were described as claystone, thick-bedded to massive, nonfissile, slightly to moderately calcareous, soft, moist, medium-gray with a slight olive tinge, dense, solid, and bedded at low angle.

The Green River Formation samples, GR/86/V33-0/2-3/1 (first batch) and GR/86/V22-0 (second batch) were from Garfield County, Colorado. They were obtained from the roof of the Colony Mine in two separate but closely adjacent drill holes. This mine is developed in the Mahogany Zone of the Parachute Creek Member. The samples were described as indurated, hard, thinly bedded calcareous marl.

The Nolichucky Shale samples were from the Joy 2 well in Oak Ridge, Tennessee, at depths of 181.0 to 181.5 m (first batch) and 181.5 to 182.0 m (second batch). From the same core, the Pumpkin Valley Shale

samples were taken at depths of 604.0 to 604.5 m (first batch) and 604.5 to 605.0 m (second batch). Both shale formations are part of the Conasauga Group, a complex sequence of Middle to Upper Cambrian clastic and carbonate strata that outcrops throughout the Valley and Ridge Province. The Nolichucky section is described from the well log as a grey-to-brown shaly siltstone with discontinuous parallel bedding. The Pumpkin Valley section is a maroon-to-grey, glauconitic, laminated, silty mudstone.

## 2.2 METHODS

Half of each core segment (split vertically) was broken with a rock hammer into small fragments (<1 cm). The fragments were pulverized for 10 min in a Siebtechnik mechanical shatterbox, consisting of an agate liner, ring, and disk (Lee et al. 1987). The resultant rock powder was sieved through 0.18-mm mesh. Any material that did not pass through the sieve was repulverized by hand, using an agate mortar and pestle, and resieved. The remaining half of each core segment was used to make thin-section or polished specimens for petrographic and electron microscopic analyses. Chemical analyses of the second-batch shales were conducted with the same analytical procedures as the first batch by staff of the ORNL Analytical Chemistry Division (Lee et al. 1987).

Particle-size distribution was measured twice (before and after complete dispersion of primary particles) by different methods. The Microtrac method (Lee et al. 1987), used before complete dispersion, provides apparent-size distribution of pulverized shales (i.e., an aggregate of primary particles is registered as the size of a single particle). The primary-particle-size distribution, which was determined after dispersive chemical treatments (geochemical fractionation), represents the true size distribution of individual primary particles.

Shales were pretreated for mineralogical analyses in the following manner. Ten grams of pulverized shales were treated with 100 mL of 1 N sodium acetate (pH = 4.5) in a warm-water bath for 24 h to remove carbonate cement for geochemical fractionation. The residue was digested by the addition of 30% hydrogen peroxide while being heated in a warm-water bath until the reaction with organics ceased. Iron

minerals and coatings were removed by washing the shale residue with sodium acetate and then treating it with sodium dithionite in three 1-g increments while stirring in 50 mL of 1 M sodium bicarbonate and 0.3 M sodium citrate solution (CBD treatment, Jackson 1975). After removal of the supernate from the centrifuge tube, the residue was filtered through a 53- $\mu\text{m}$  sieve. The <53- $\mu\text{m}$  fraction was further separated into 53 to 2, 2 to 0.2, and <0.2- $\mu\text{m}$  size fractions by the centrifugation method (Jackson 1975).

X-ray powder diffraction (XRD) analyses were performed on samples of different grain-size fractions using a Phillip's powder X-ray diffractometer. Samples were prepared for analysis by transferring potassium- or magnesium-saturated slurries of each of the size fractions to glass slides, air drying them, and then bombarding them with copper K alpha radiation through 2 theta angles from 2 to 60° in the diffractometer. The potassium-saturated samples were heated to 550° C after the initial XRD, and the magnesium-saturated samples were glycolated before being run again to further identify minerals.

The 50-g samples of the pulverized Pierre and Pumpkin Valley shales and reference montmorillonite were each suspended in 200 mL of "concentrated brine solution" used in the Radionuclide Sorption Task of the SERP. The suspended samples were boiled in a 500 mL flat-bottom flask with refluxing condenser. After 100 d of continuous boiling, 50 mL of the suspensions was taken from the flasks and passed through 0.45  $\mu\text{m}$  Acrodisc filters to collect leachates for chemical analyses and solids for X-ray diffraction and microscopic analyses. The leachates were sent to the ORNL Analytical Chemistry Division for chemical analyses by Environmental Protection Agency Procedure (200.7).

For high-resolution transmission electron microscopic analysis, calcium saturated, 2- to 5- $\mu\text{m}$ -size fractions of the reference clays were prepared. A small amount of each sample was placed in a 50-ml plastic centrifuge tube. Approximately 10 mL of glycol methacrylate (GMA, SPI Supplies) was added to the sample before the resin was allowed to saturate the clays overnight. After removal of excess GMA by centrifugation and decantation, about 5 mL of prepolymerized GMA was added to and mixed with the sample and dispersed clays in the resin via

sonification. The clay and prepolymerized GMA mixture was centrifuged for 30 min (at 24,000 rpm) to concentrate the clays in the bottom of the centrifuge tube. The centrifuge tubes were placed in a 50°C vacuum oven at -15 kPa. One to three days were required for hardening of the resin. The GMA resin block resembled a truncated cone with the clays concentrated in and oriented parallel to the tip-end. The cone was then placed in a small amount of epoxy resin with the tip-end down to provide a workable-size substrate for cutting and trimming.

The GMA block was cut with a fine-blade coping saw and filed to a rectangular shape measuring approximately 15 x 7 x 7 mm. Care was taken to keep the clay layer parallel to the top of the block and near its front. The rectangular block was mounted in a microtome trimming holder and trimmed with a very fine file and razor blade so that the front edge (the edge to be cut) was a trapezoid with a base <1.5 mm across, with the clay layer above the midpoint of the face. The trimmed face was sectioned using an ultramicrotome with a diamond knife. Thin sections having thicknesses <100 nm, judged from the interference color (silver), were collected on carbon coated grids. The specimens were coated with carbon and examined using a JEOL JEM-2000FX transmission electron microscope (TEM), with KEVEX energy dispersive X-ray spectrometer system for elemental analysis.

### 3. RESULTS AND DISCUSSION

#### 3.1 PHYSICAL PROPERTIES

Apparent-size distributions and surface areas of both first and second batches of the pulverized samples were measured and the results are presented in Table 1. The apparent-size distributions in the two batches were reasonably similar in spite of the fact that they were prepared at different times and from different core segments. The apparent-size distribution is controlled by conditions of the laboratory pulverization process and degree of shale diagenesis. Because the laboratory processes were approximately standardized in terms of grinding time and equipment, the differences of the apparent-size distribution are interpreted to be related to the degree of compaction and cementation during diagenesis and metamorphic processes.

The surface areas of the pulverized Chattanooga Shale and Pumpkin Valley Shale were significantly different (5 vs 13  $\text{m}^2/\text{g}$ , respectively) even though both shales have similar apparent-particle-size distributions. The results suggest that the nitrogen gas, used for surface area measurement, was able to penetrate into the coarser particles ( $>2.8 \mu\text{m}$ ) of the Pumpkin Valley Shale but not into the similar-size particles of the Chattanooga Shale. This particular finding has an important implication for the interpretation of results of geochemistry experiments relating to the kinetics of rock-water and rock-radioluclide interactions.

To extrapolate the laboratory crushed-rock experimental results to field conditions to assess performance, the validity of surface area data should be examined for the particular rock sample. The ultramicropore surface included in the gas-penetration measurement may not be an active site for radionuclide sorption. Primary-particle-size distributions for both first and second batches were determined after geochemical fractionation (Table 2). There were some differences in size distribution between the two batches, but they are minor, considering the difficulties in obtaining reproducible results that are inherent to the methodology. Disaggregation of the Chattanooga Shale

Table 1. Apparent-size distribution and surface-area measurement of pulverized shales (<180  $\mu\text{m}$ )

	Apparent-size distribution (%)				Surface area			
	180-53 $\mu\text{m}$		53-2.8 $\mu\text{m}$		<2.8 $\mu\text{m}$		(m <sup>2</sup> /g)	
	1st <sup>a</sup>	2d <sup>a</sup>	1st	2d	1st	2d	1st	2d
Chattanooga Shale	24	27	66	64	10	9	4.8	4.4
Pierre Shale	0	1	81	81	19	18	21.9	23.8
Green River Formation	13	20	74	68	13	12	1.9	2.0
Nolichucky Shale	18	2	67	72	15	26	17.1	13.3
Pumpkin Valley Shale	18	28	69	61	13	11	12.9	12.4

<sup>a</sup>1st and 2d are sample batch numbers.

Table 2. Primary-particle-size distribution after geochemical fractionation of pulverized shales

	Size distribution (%)							
	180-53 $\mu\text{m}$		53-2 $\mu\text{m}$		2-0.2 $\mu\text{m}$		<0.2 $\mu\text{m}$	
	1st <sup>a</sup>	2d <sup>a</sup>	1st	2d	1st	2d	1st	2d
Chattanooga Shale	1	0	64	66	26	24	9	10
Pierre Shale	1	0	31	29	19	26	50	45
Green River Formation	1	0	54	58	14	14	32	28
Nolichucky Shale	1	3	49	54	21	17	30	26
Pumpkin Valley Shale	7	8	63	67	18	15	12	10

<sup>a</sup>1st and 2d are sample batch numbers.

was more difficult than the other shales. The presence of clay minerals or carbonate minerals in the 53- to 2- $\mu\text{m}$  fraction of the shales indicates that the primary-particle fractionation was incomplete (see 3.5 Mineralogical Properties). It appears that a better fractionation procedure should be developed for individual shales because geochemical fractionation is a process of mineralogical separation that provides information for only semiquantitative mineralogical analyses.

As part of physical characterization of the shales, other data such as bulk density and porosity are needed for performance analyses, but these were not planned for this year's activity.

### 3.2 CHEMICAL PROPERTIES

The chemical compositions of the first and second batches of the shale samples, analyzed by wet chemical methods, are summarized in Table 3. The chemical analysis data provide only supplemental information for mineralogical analysis. However, the chemical data are a sensitive parameter for the evaluation of spatial uniformity of the samples taken from different cores and different segments of a core.

The chemical composition of the second batch of the Chattanooga Shale was similar to the first batch, except that the second batch had higher iron and sulfur contents, suggesting the presence of a higher pyrite content in the second batch. The second batch of the Pierre Shale had lower silica content and higher calcium content than the first batch, indicating that the second batch had a lower quartz and a higher calcite content. However, the carbonate content in the second batch did not substantiate such a noticeable increase in calcite. Lower silica and aluminum contents and higher magnesium, calcium, and carbonate contents in the second batch relative to the first batch of the Green River Formation suggested that the second batch had higher amounts of dolomite and a lower content of aluminosilicate minerals. The summations of chemical components for the Nolichucky Shale were substantially lower than for the other shales, and this was even more noticeable in the second batch of the Nolichucky Shale. Although the Nolichucky Shale had considerable amounts of chlorite, weight

Table 3. Chemical composition (wt%) of the first and second batches of whole-rock samples<sup>a</sup>

	Chattanooga Shale		Pierre Shale		Green River Formation		Nolichucky Shale		Pumpkin Valley Shale	
	1st <sup>b</sup>	2d <sup>b</sup>	1st	2d	1st	2d	1st	2d	1st	2d
SiO <sub>2</sub>	57.8	55.6	49.2	38.5	34.2	40.7	40.7	36.4	62.1	64.2
Al <sub>2</sub> O <sub>3</sub>	13.6	12.5	14.0	12.1	7.6	9.3	13.0	13.0	20.8	18.1
K <sub>2</sub> O	3.9	3.9	2.3	1.7	3.2	3.1	3.4	3.5	5.4	4.1
Na <sub>2</sub> O	0.4	0.6	0.7	0.8	0.7	1.8	0.3	0.5	0.7	0.8
FeO	5.8	8.8	5.4	5.2	2.7	3.4	4.0	3.7	6.7	6.7
TiO <sub>2</sub>	0.8	0.5	0.5	0.4	0.3	0.3	0.5	0.4	0.8	0.6
MgO	1.3	1.1	2.2	1.7	6.4	5.6	2.3	2.3	2.0	1.7
CaO	0.3	0.7	8.6	16.8	13.6	11.2	6.0	2.0	0.3	0.5
CO <sub>3</sub>	0.5	0.0	10.5	11.9	26.4	22.1	9.6	4.5	0.5	0.7
S	<u>4.3</u>	<u>6.2</u>	<u>0.9</u>	<u>1.6</u>	<u>0.3</u>	<u>0.5</u>	<u>0.1</u>	<u>0.1</u>	<u>0.3</u>	<u>0.2</u>
Total <sup>c</sup>	94.1	89.9	94.3	90.7	95.4	98.0	79.9	66.4	99.9	97.6

<sup>a</sup>Chemical composition is based on weight after 105° C treatment for 24 h.

<sup>b</sup>1st and 2d are sample batch numbers.

<sup>c</sup>Differences from 100% are organic matter, structural water, and other trace components.

contribution by chlorite structural water (hydroxyl water) would be less than 3% (assuming 20% chlorite in the sample). The silica, calcium, and carbonate contents of second batch were unreasonably low. Therefore, both the first and second Nolichucky Shale batches were resubmitted for chemical analysis (results are available). There were only minor differences in chemical composition between the first and second batches of the Pumpkin Valley Shale.

The results of first- and second-batch chemical analyses indicate that although measurable differences in chemical composition exist, these batch differences were not considered important when compared with the differences in chemical compositions among the end-member shales. Furthermore, for any given major mineral components, the differences between two batches were <4% when the differences of the mineralogical composition were estimated from the differences of the chemical compositions. The significance of compositional differences between the first and second batches has not been carefully evaluated in this study. However, radionuclide sorption experiments did not show noticeable differences in sorption values between the two batches (Meyer et al. 1987 and 1988).

### 3.3 MINERALOGICAL PROPERTIES

Mineralogical properties of the first batch of the selected shales were examined by petrographic microscopy, back-scattering mode scanning electron microscopy, thermal analysis, and X-ray diffraction analysis in FY 1987 (Lee et al. 1987). In FY 1988, the mineralogical characterization activity concentrated on X-ray diffraction analysis of the second-batch samples. X-ray diffraction analysis is the simplest and most reliable method to help confirm the chemical analysis results.

The X-ray diffraction analyses of randomly oriented whole-rock samples of the Chattanooga batches indicated that quartz (0.423-nm d-spacing peak) and illite (0.1 nm) were the major mineral components, and feldspars (0.32 nm) and pyrite (0.27 nm) were minor components (Fig. 1). There were no significant differences in the pyrite peak

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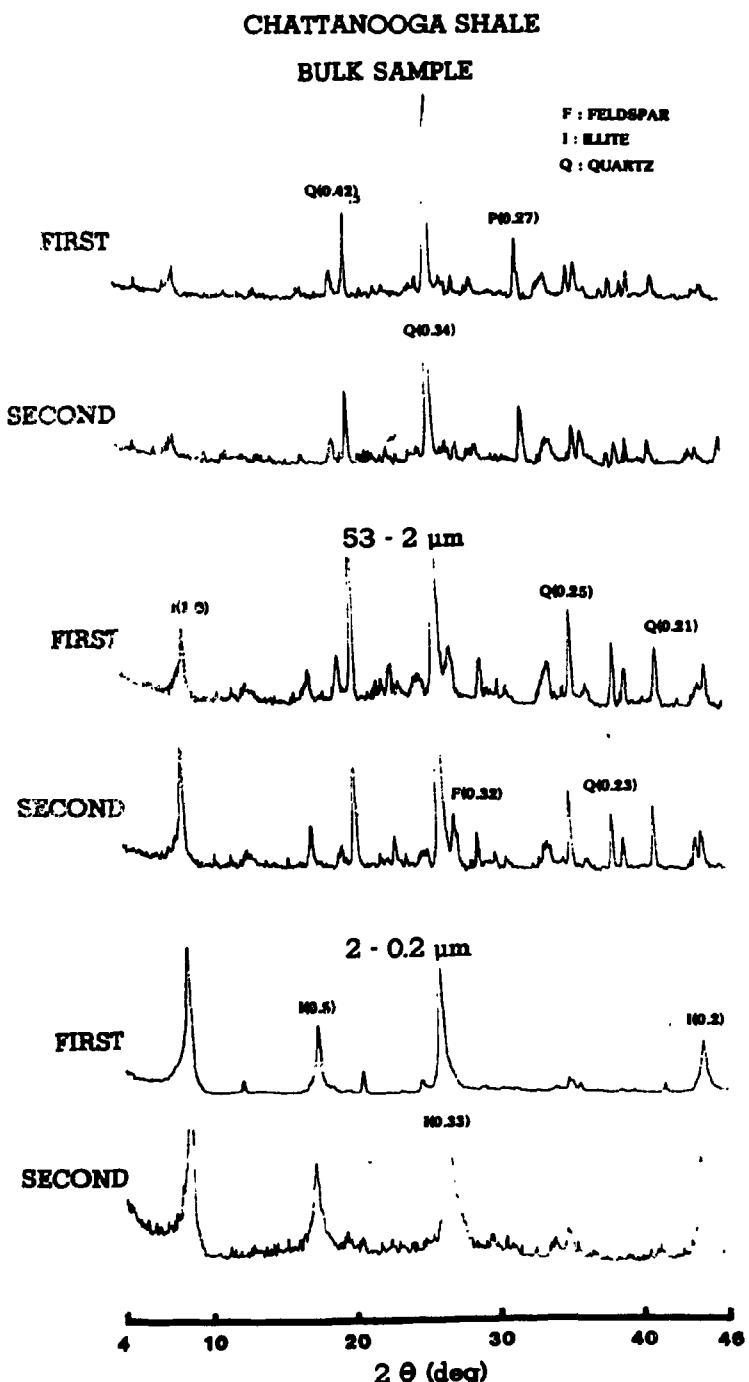


Fig. 1. X-ray diffractograms of first and second batches of the Chattanooga Shale (d-spacing values are in nanometers).

intensities between the first and second batches, although the chemical analyses indicated that the second batch might have a 2 to 4% higher pyrite content than the first batch (Table 2). The X-ray diffraction method was not sensitive enough to detect this difference in pyrite content. Differential thermal analysis or differential scanning calorimetric analysis would be a more sensitive method for pyrite analysis if one were able to suppress organic matter interferences. After geochemical fractionation, the intensity ratio of micaceous minerals (micas and illite) to quartz suggested that quartz was the major component and micaceous minerals were the minor component in the silt (53 to 2  $\mu\text{m}$ ) fraction but illite was the major component in the clay ( $<2 \mu\text{m}$ ) fraction of both batches. The coarse clay (2 to 0.2  $\mu\text{m}$ ) fraction had a small amount of kaolinite (0.71 nm) and quartz. The fine clay fractions ( $<0.2 \mu\text{m}$ ) did not contain either kaolinite or quartz.

The X-ray diffraction analyses of the second batch of the Pierre Shale showed the presence of calcium-smectite (1.2 nm), micaceous minerals, kaolinite, quartz, calcite, and pyrite (Fig. 2). After geochemical fractionation, quartz was the major component and smectite, micas, and kaolinite were minor components in the silt-size fraction. The coarse-clay fraction had smectite as the major component and kaolinite, mica, and quartz as minor constituents. Both mica and quartz were absent in the fine clay. The absence of the 1.0-nm peak in the fine-clay fraction suggested that the 1.0-nm peak in the coarse-clay fraction was detrital muscovite rather than illite. Calcium smectite was the dominant mineral in the fine-clay fraction. The presence of a very small amount of kaolinite was confirmed by the disappearance of the 0.71-nm peak after heat treatment of the potassium-saturated fine-clay sample. There were no differences between the X-ray diffraction patterns of the first and second batches, even though samples were obtained from different cores at different locations. The differences in calcium content observed from the chemical analyses were not detected by bulk X-ray diffraction analyses.

The second batch of the Green River Formation was very similar in mineralogical composition to the first batch from this formation

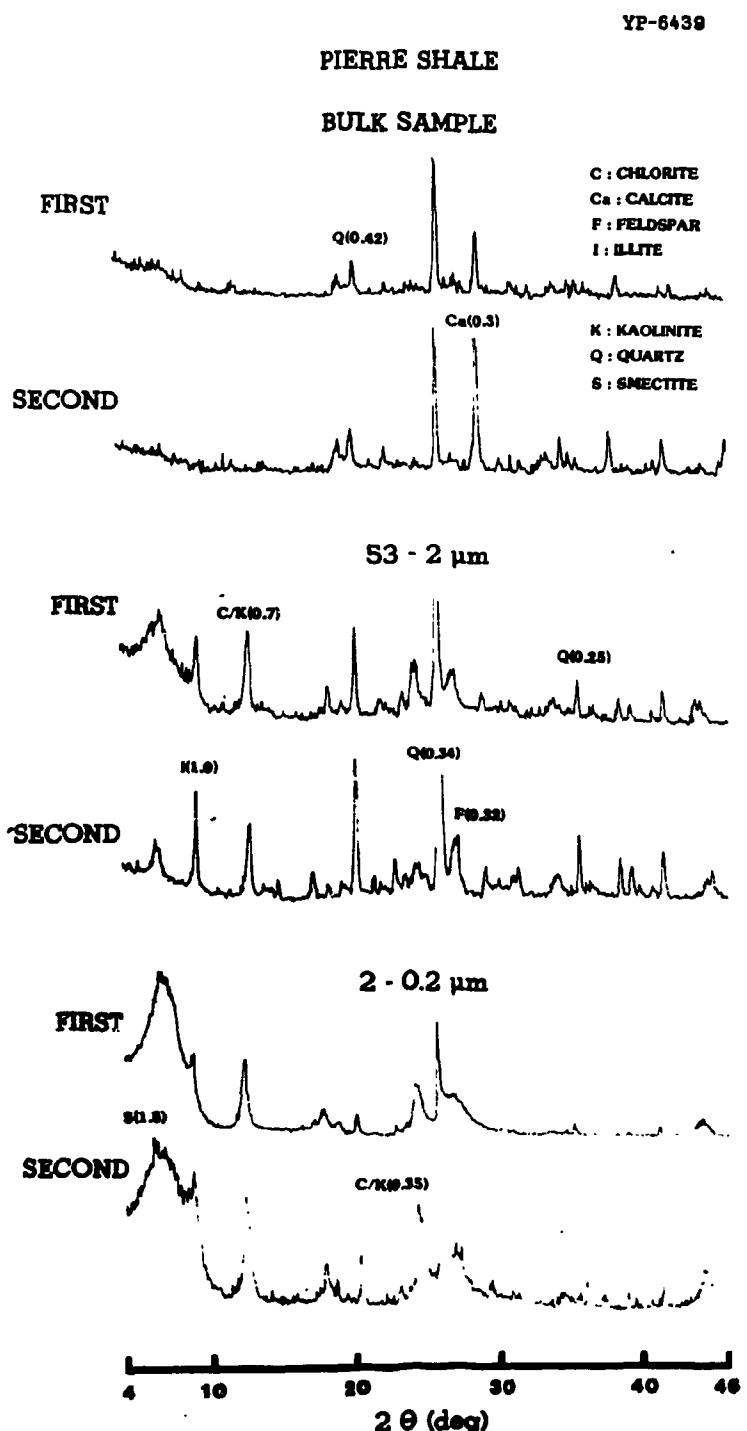


Fig. 2. X-ray diffractograms of first and second batches of the Pierre Shale (d-spacing values are in nanometers).

(Lee et al. 1987). X-ray diffraction analyses of the bulk sample showed that dolomite (0.29 nm) was the major mineral component and quartz was a minor component (Fig. 3). After geochemical fractionation, dolomite and quartz were the dominant components and feldspars were the minor component in the silt fraction. The peak intensity of quartz and feldspars increased relative to the intensity of dolomite in the coarse-clay fraction. On the other hand, illite and quartz were the major mineral components in the fine-clay fraction. The X-ray diffraction analysis results indicated that the geochemical fractionation method, developed for aluminosilicate-rich samples, was not adequate for removing all of the dolomite in the Green River Formation samples.

The results of X-ray diffraction analyses of the second batch of the Nolichucky Shale indicated that illite and quartz were the major bulk sample mineral components, which confirmed results from the first batch (Fig. 4). Minor components were calcite, chlorite, kaolinite, and feldspars. Contradicting the chemical analyses, the bulk sample X-ray diffraction pattern showed that the calcite peak intensity of the second batch was higher than that of the first batch. After geochemical fractionation, quartz was the most abundant but there were considerable amounts of illite and chlorite in the silt fraction. The chemical analysis also confirmed that the 0.71-nm peak observed from diffraction patterns corresponded to the second-order *d*-basal spacing (002) of chlorite rather than the first-order (001) of kaolinite. The quartz content decreased as the illite content increased, and the chlorite content remained unchanged in the coarse-clay fraction in comparison with the silt fraction. Illite was the most abundant mineral in the fine-clay fraction.

The mineralogy of the second batch of the Pumpkin Valley Shale, an illitic end-member, was similar to that of the first batch. Illite and quartz were the most abundant minerals in the bulk sample (Fig. 5). The sand fraction of the sample was mainly quartz with barely detectable amounts of illite and chlorite (chlorite plus kaolinite). However, illite and chlorite were the dominant minerals in the silt and clay fractions. Chlorite was more abundant in the silt and coarse-clay

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## GREEN RIVER FORMATION

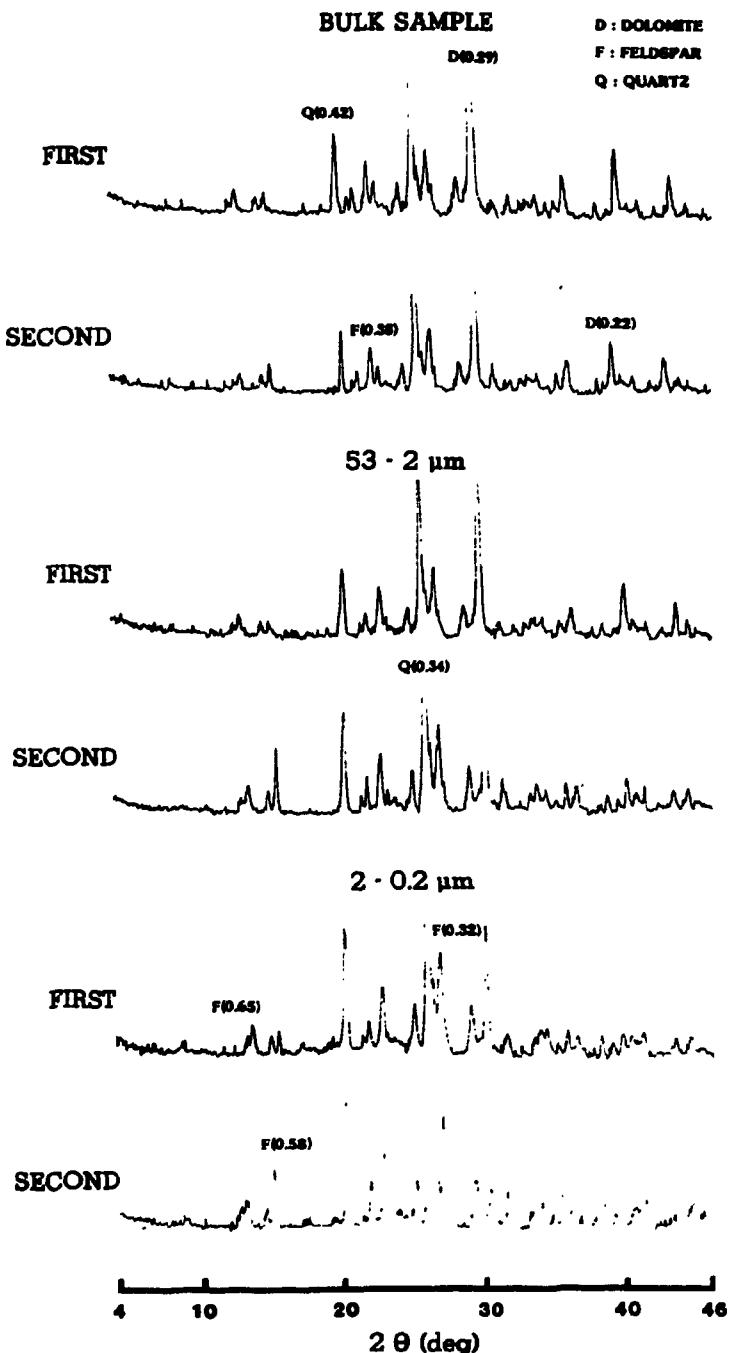


Fig. 3. X-ray diffractograms of first and second batches of the Green River Formation (d-spacing values are in nanometers).

YP-6441

## NOLICHUCKY SHALE

## BULK SAMPLE

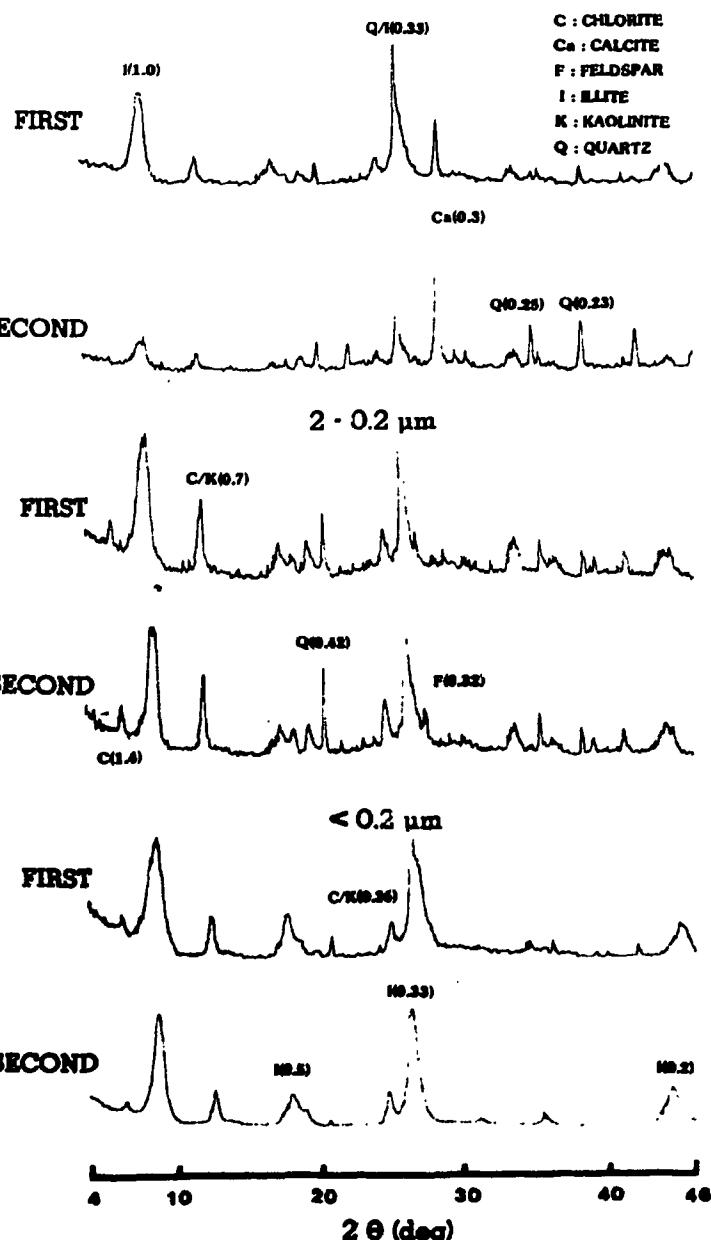


Fig. 4. X-ray diffractograms of first and second batches of the Nolichucky Shale (d-spacing values are in nanometers).

YP-6442

## PUMPKIN VALLEY SHALE

**BULK SAMPLE**

C : CHLORITE  
I : ILLITE  
K : KAOLINITE  
Q : QUARTZ

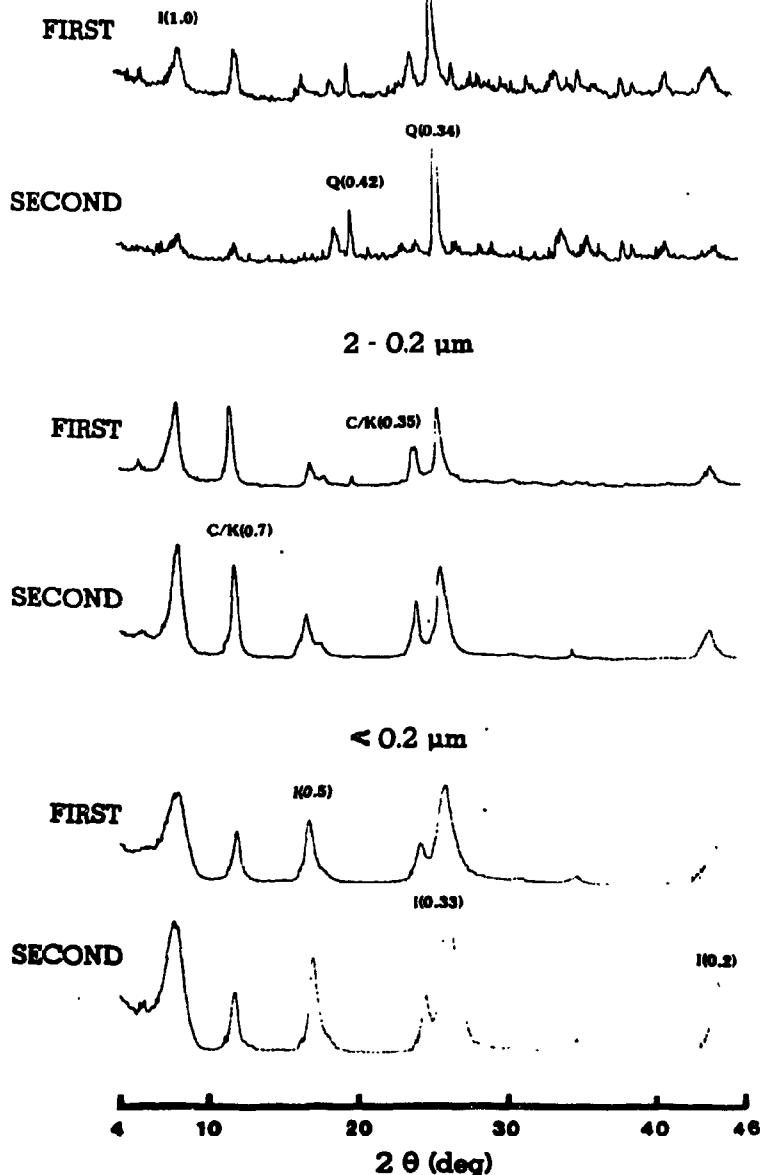


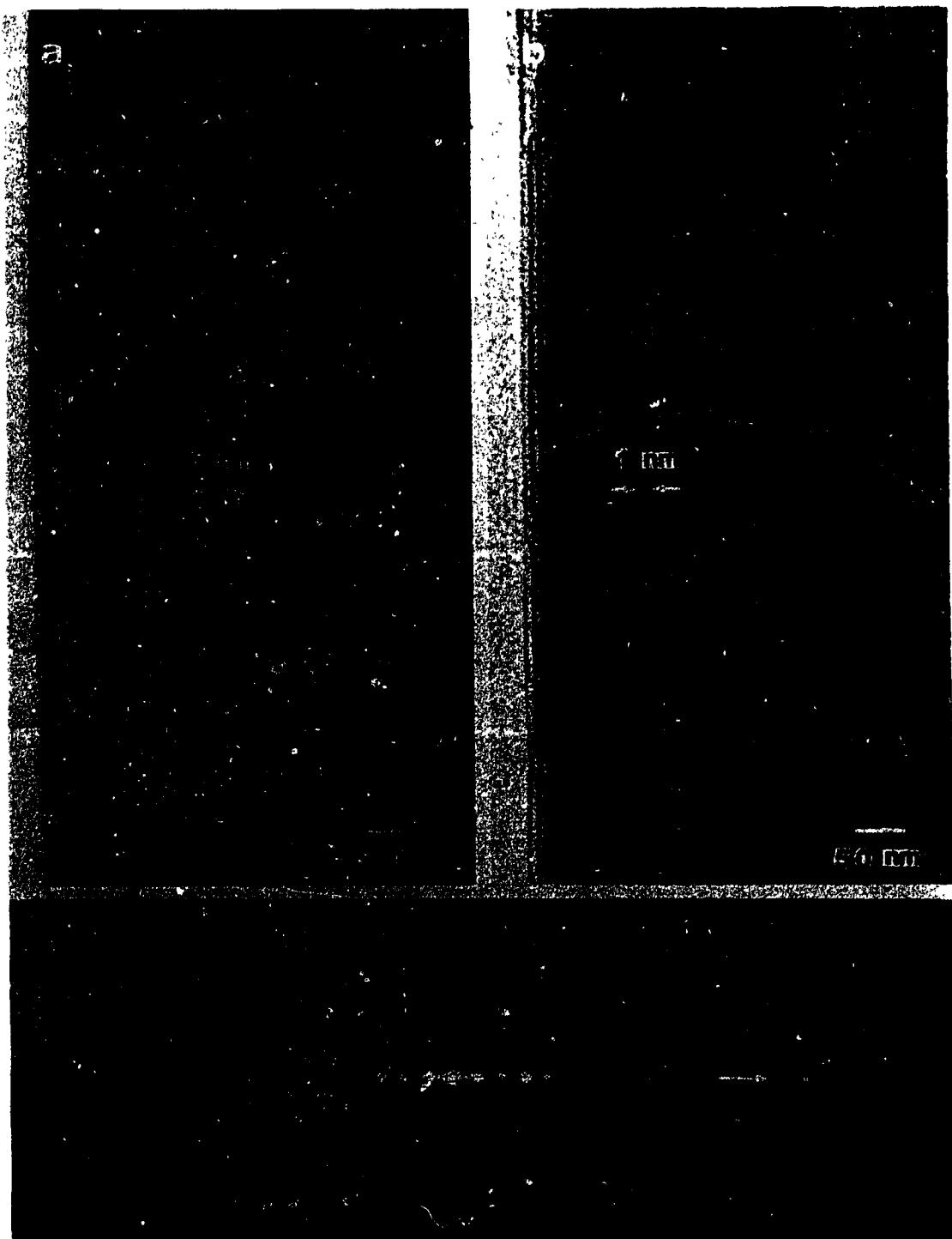
Fig. 5. X-ray diffractograms of first and second batches of the Pumpkin Valley Shale (d-spacing values are in nanometers).

fractions than in the fine-clay fraction. Although the presence of chlorite in the samples contributed to the intensity of the 0.71-nm peak, the presence of kaolinite in the sample was detected by the reduction in intensities of the 1.4- and 0.71-nm peaks observed after heat treatment of the fine-clay fraction. The abundance of kaolinite in the Pumpkin Valley Shale was the most noticeable difference from the Nolichucky Shale. As indicated by the chemical analysis results (Table 2), no measurable differences in mineralogy between the second and first batches of the Pumpkin Valley Shale were observed.

### 3.4 HIGH-RESOLUTION ELECTRON MICROSCOPY

High-resolution transmission electron microscopy (HRTEM), including energy dispersive X-ray spectrometry (EDX), of undisturbed shale samples provides crucial information on mineral composition, crystal structure, matrix composition, and micromorphology that cannot be determined by other techniques. In FY 1987, preliminary HRTEM examinations of the first-batch end-member shales were completed and described in the progress report for that year (Lee et al. 1987).

This year (FY 1988), several reference mineral samples, such as biotite (1.0-nm lattice fringes), chlorite (1.4 and 0.7 nm), calcium-montmorillonite (1.2 nm), and kaolinite (0.7 nm), were prepared for both microscope and X-ray analyzer calibrations. The biotite specimen showed many well-defined 1.0-nm lattice fringes at an under-focus condition (-36 steps from minimum-contrast position) (Fig. 6a) and a less-clear fringe image at minimum-contrast (on-focus) condition (Fig. 6b). The fringe image was not clear in some areas, even at the under-focus position. The localized minimum contrast could be the result of microtopographic changes, electron beam damage, or structural disorder. The step-wise image focus tests indicated that the lattice fringe space was not significantly altered under a wide range of under- and over-focus conditions but lost contrast under the out-of-focus conditions. Selected area diffraction patterns of the area examined by HRTEM also showed a series of biotite (001) diffraction spots on the C\* axis (Fig. 6c). EDX analysis of the same area as well as other areas showed



**Fig. 6.** High-resolution transmission electron micrographs of biotite: (a) on-focus position, (b) 36 steps under-focus position, and (c) selected area electron diffraction pattern.

that silica, aluminum, iron, magnesium, and potassium were major elemental constituents and titanium and manganese were minor components of the biotite (Fig. 7). The copper peaks in the spectrum were derived from the grid supporting the specimen in the sample chamber. The chemical composition of the biotite will be calculated by thin film approximation and compared with electron microprobe analyses.

The HRTEM of chlorite showed strong first-order 1.4-nm lattice fringes with weaker second-order 0.7-nm fringes between the first-order fringes (Fig. 8). The intensity of the second-order fringes changed from one area to another, but spacing changes did not occur during focusing changes. EDX analysis showed that silica, magnesium, aluminum, and iron were major components of the chlorite (Fig. 9). Thin-section specimens of calcium-montmorillonite and kaolinite were prepared but were not examined by the HRTEM in this reporting period.

The results of the reference sample analyses demonstrated that detection of lattice fringes spaced from 0.7 to 1.4 nm under a given focusing condition is possible for sedimentary rocks containing several different layer-silicate minerals. The HRTEM method will be applied to smectite alteration studies in the future.

### 3.5 CLAY MINERAL TRANSFORMATION IN 100°C AQUEOUS SOLUTION

Clay minerals in shales are expected to be altered under hydrothermal conditions and can be significantly affected by minor changes in temperature, leading to changes in rock strength, porosity, and permeability (Hansen and Vogt 1987). Therefore, it is important to examine clay mineral behavior in a repository environment because emplacement of waste will increase the temperatures of the host rock, backfill material (smectite), and groundwater. The boiling experiment with Wyoming montmorillonite, Pierre Shale, and Pumpkin Valley Shale in a brine solution does not simulate exact near-field repository conditions by any means, but it is a simple approach to a preliminary assessment of hydrothermal effects on clay minerals and groundwater composition.

YP-6500

16-Aug-1989 15:22:17

Biotite

Vert = 2000 counts Disp = 1

Preset =

Elapsed = 2594 secs

Si

O

Al

Mg

K

Fe

Cu

Cu

Ti

Mn

Fe

← 0.000 Range = 10.230 keV →  
Integral 0 = 3893050

Fig. 7. Energy dispersive X-ray analysis spectrum of microscopically studied area of biotite specimen.

YP 6503

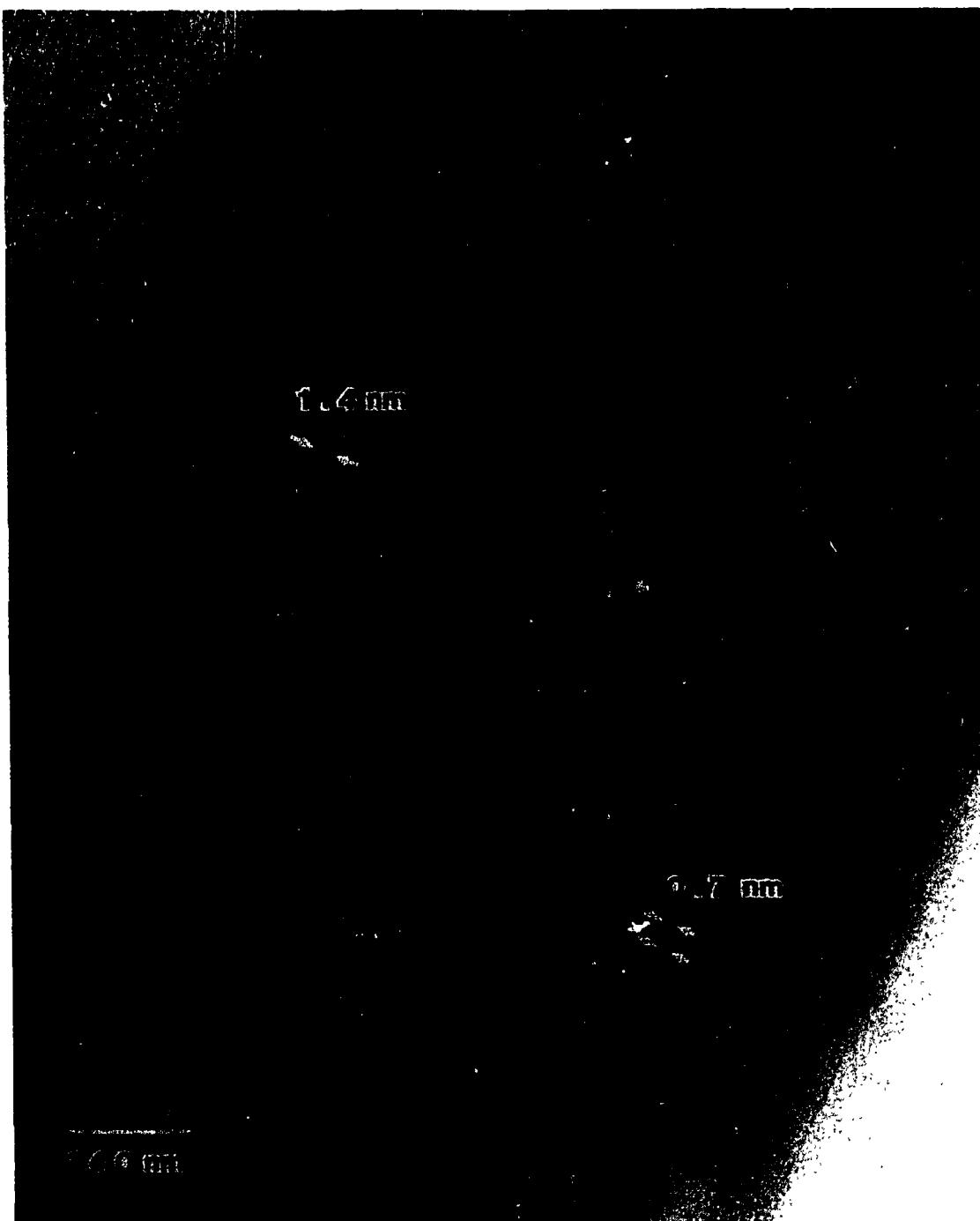


Fig. 8. High-resolution transmission electron micrograph of chlorite specimen.

YP-6501

17-Aug-1989 14:40:48

chlorite

Vert= 500 counts Disp= 1

Preset= Off

Elapsed= 120 secs

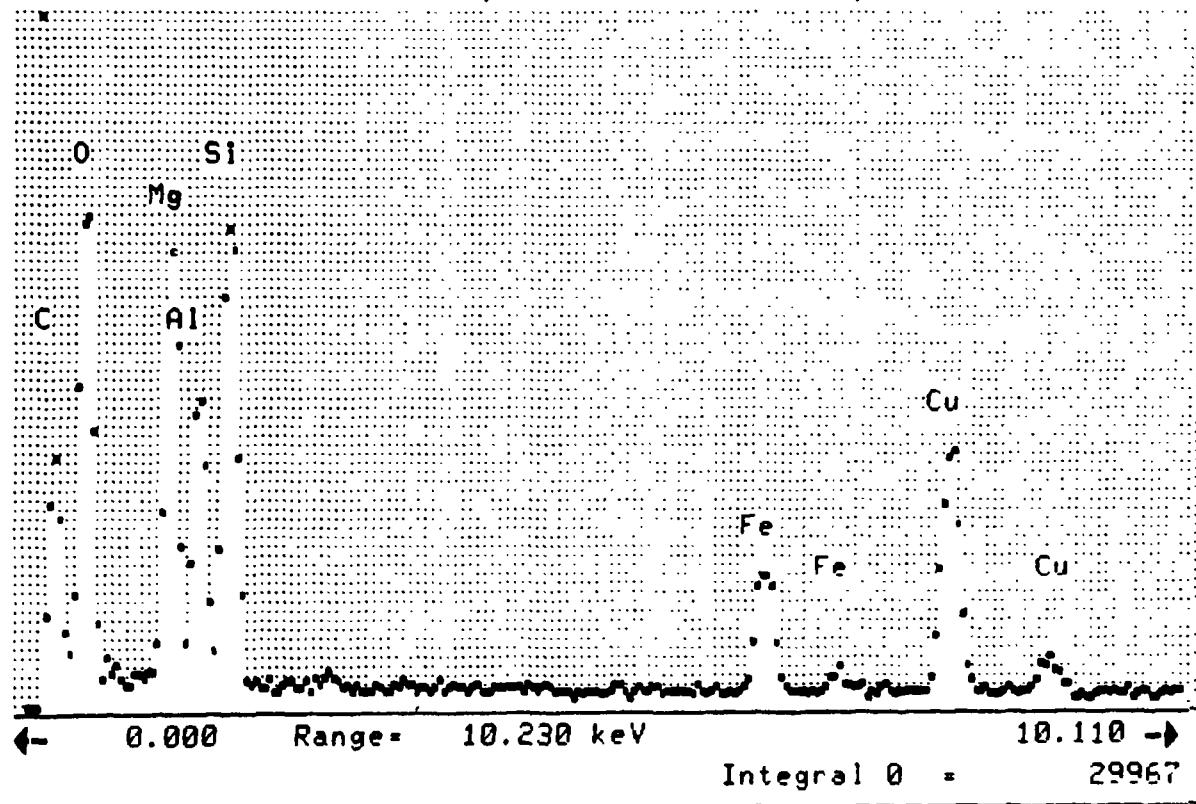


Fig. 9. Energy dispersive X-ray analysis spectrum of microscopically studied area of chlorite specimen.

Chemical analyses of leachate solutions after 100 days of the boiling experiment showed significant differences in composition from the brine solution used for leaching (Table 4). The synthetic brine solution was prepared on the basis of groundwater composition from a test well located in the Conasauga Group (Meyer et al. 1987). Leachates of both the Wyoming montmorillonite and Pumpkin Valley Shale had lower concentrations of most cations (except silica and boron) and anions than the initial brine solution. The leachate of the Pierre Shale had a higher concentration of boron, calcium, silica, carbonate, and sulfate. The results suggest that both precipitation and dissolution processes are taking place during the boiling experiments. Preliminary results from X-ray diffraction analyses showed no detectable amounts of new mineral phases nor any changes in mineral distribution (detection limit, about 5 wt%). The results will be further evaluated by the EQ3NR/EQ6 computer program (Wolery 1983) for geochemical aqueous speciation-solubility calculations. The boiling experiment will continue to 250 d, and both solution and solid phases will be analyzed again to measure hydrothermal effects on mineral composition, stability, and transformation.

Table 4. Chemical composition (mg/L)<sup>a</sup> of leachate solutions after 100 d of clay boiling experiment

	Wyoming montmorillonite	Pierre Shale	Pumpkin Valley Shale	Brine solution
Al	20	38	25	33
B	62	250	180	<8
Ba	0.4	0.4	43	<0.2
Be	0.6	0.6	0.6	0.6
Ca	5000	12000	7700	8800
Fe	<2	<2	23	<2
K	500	680	780	840
Li	<20	<20	27	27
Mg	940	<1	2000	2600
Mn	2.5	<0.5	18	<0.5
Na	19000	36000	36000	43000
Si	60	26	100	<20
Sr	560	570	570	570
Br	360	540	480	680
CO <sub>3</sub>	7.5	600	2.5	2.5
Cl	47000	72000	72000	100000
F	56	120	94	150
SO <sub>4</sub>	<250	690	<250	<250
pH (after)	6.9	6.6	6.9	5.3
pH (before)	6.4	8.2	4.8	5.2

<sup>a</sup>pH given in pH units.

## 4. SUMMARY

Five end-member shale samples were used in the SERP investigation: the Chattanooga Shale from Fentress County, Tennessee; the Pierre Shale from Gregory County, South Dakota; the Green River Formation from Garfield County, Colorado; and the Nolichucky Shale and Pumpkin Valley Shale from Roane County, Tennessee. The results of detailed morphological and mineralogical analyses of the first batches of the shales were reported in the FY 1987 progress report (Lee et al. 1987). It was necessary to prepare a second batch for additional analyses and sorption studies because all of the first batch was used in earlier experiments. The second-batch samples of the Chattanooga Shale, Nolichucky Shale, and Pumpkin Valley Shale were obtained from the same cores used for the first batch. However, the second-batch samples of the Pierre Shale and Green River Formation were prepared from different cores obtained from the same locations as the first cores.

The objectives of these studies were to characterize the second batch of the end-member shales and to compare the acquired data with the results of the first-batch characterization studies. In addition, two new experiments, high-resolution transmission electron microscopy (HRTEM) for reference minerals and clay-boiling experiments for smectitic and illitic samples, were initiated in this study. HRTEM is a valuable tool for clay transformation studies, and the clay-boiling experiment is a simplified approach to analyze hot-brine-altered clays under a near-field repository condition.

The results of physical characterization studies showed that the first batch and second batch of each end-member shale had different apparent size distributions but very similar primary-particle-size distributions. For apparent-size distribution, the Nolichucky Shale had the largest difference (16% for 180 to 53  $\mu\text{m}$  fraction) between the first batch and second batch and the Pierre Shale had the least difference (1%) between two batches. The Nolichucky Shale had a large difference in surface area (22%) between the two batches. However, the first and

second batches of the end member shales had similar primary-particle-size distributions.

The results of first- and second-batch chemical analyses showed that although there were measurable differences in chemical composition, these differences were not considered important when compared with the differences in chemical compositions among end-member shales. When the chemical differences of the two batches were converted to equivalent mineral contents, the differences were <4% (pyrite in the Chattanooga Shale and calcite in the Pierre Shale). There were some problems with the analytical data - particularly both batches of the Nolichucky Shale. The Nolichucky Shale samples were resubmitted to the Analytical Chemistry Division, but the results are not available.

As expected, the results of X-ray diffraction analyses indicated that the second batches of the shales were very similar in mineralogical composition to the first batches. In the clay-sized fraction, illite was the major component of the Chattanooga Shale, Nolichucky Shale, and Pumpkin Valley Shale, whereas dolomite was the dominant component in the Green River Formation, and smectite (calcium montmorillonite) was the major component in the Pierre Shale. Silt-size (53 to 2  $\mu\text{m}$ ) quartz was the second major mineral in the shales, with the exception of the Pierre Shale, which had at least an equal amount of calcite.

HRTEM with energy dispersive X-ray spectroscopy for reference samples (micas, chlorite, smectite, and kaolinite) is in progress. The micrographs of ultramicrotome thin sections of biotite and chlorite showed a series of well-defined (001) lattice fringes. The biotite specimen showed 1.0-nm fringe spaces with reproducible silica, aluminum, iron, magnesium, and potassium spectra. The chlorite specimen showed 1.4-nm fringes with silica, magnesium, aluminum, and iron spectra.

Chemical analyses of samples of the Wyoming montmorillonite, Pierre Shale, and Pumpkin Valley Shale leachates, obtained after 100 d of boiling in a synthetic brine solution, indicated that some cations and anions were removed from the brine solution through sorption and

precipitation and others were released from minerals through dissolution. However, preliminary X-ray diffraction analyses did not show detectable amounts of new mineral phases or changes in mineral distribution. The boiling experiment will continue to 250 d. Analyses of both solution and solid phases will be conducted to measure hydrothermal effects on clay mineral transformations.

In conclusion, the differences in selected physical, chemical, and mineralogical properties between the first batches and second batches were not considered important enough to warrant further characterization of the second batch. Other mineralogical characteristics, such as micromorphology and thermal properties investigated in FY 1987 for the first batches, can be applied to the second batches of the end-member shales. The results of this study suggest that compositional differences between the two batches are not large enough to affect the results of other studies, such as radionuclide sorption and organic matter characterization. Because HRTEM is a valuable tool for clay mineral transformation studies, fringe spacing calibration and quantitative elemental analysis for reference minerals will continue. The results of smectitic and illitic clay-boiling experiments are not conclusive, but the changes in leachate composition warrant comprehensive investigation of mineralogical compositions and their physicochemical properties after 250 d of boiling.

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