

## Chapter 2

# Mineralogy and Geochemistry of the Ciniza Lake Beds, and Related Strata

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### INTRODUCTION

Sixteen samples from the Ciniza Lake Beds and associated strata were analyzed by X-ray diffraction for gross mineralogy and mineralogy of the clay-size fraction. In addition, the amounts of organic matter, calcium carbonate, acid-soluble cations, and some minor elements in the samples were analyzed. Ten samples (FW1-2a-2j) are from the sequence collected every 15 cm through the vertical extent of the lake beds at locality FW1 (chap. 1, figs. 4, 17). One sample (FW1-1) came from the sandstone matrix in the flat-lying conglomerate that directly underlies the lake beds at locality FW1 and elsewhere in the area. Another sample (FW6-2) is from a limestone pebble from the same bed of conglomerate at locality FW6. One sample (FW6-3) came from the principal fossil plant locality in the lake beds at FW6, and another came from the lake beds at FW5. A sample of structureless mudstone from the main body of the Monitor Butte Member at locality FW8, which appears to have been deposited in a stream channel contemporaneous with Lake Ciniza, was also analyzed for comparison with the lake bed samples.

### METHODS

The samples were subsampled and crushed in a SPEX Mixer Mill to a fine powder. Percent organic matter and carbonate were determined by controlled loss on ignition at 550 and 1000° C, respectively (Dean 1974). The percent of inorganic, noncarbonate elastic fraction was taken as the difference between 100 percent and the sum of organic and carbonate percentages.

Soluble, or exchangeable, cations were extracted in 1.0 N ammonium acetate at pH 5.2 (Wangersky and Joensuu 1968). The amounts of Ca, Mg, Mn, and Fe dissolved in the ammonium acetate were determined with a Unicam SP-90 Atomic Absorption Spectrophotometer.

Total amounts of Mg, Fe, and Mn in the samples were also determined by atomic absorption. Samples for total analyses were prepared by digesting 500 mg of sample, ashed at 1000° C, successively in concentrated HNO<sub>3</sub>, concentrated HF, and 1.0 N HCl. The samples were evaporated to dryness before the addition of each acid. The final dried residues were extracted in 1.0 N HCl, and brought to 100 ml total volume with distilled water. One percent lanthanum was added to each of the final solutions to suppress interferences due to silica and alumina.

Untreated powdered samples mounted with random grain orientations on glass slides were used for X-ray diffraction analyses of gross mineralogy. Samples were analyzed with a General Electric XRD-5 X-ray Diffractometer using Ni-filtered Cu-K  $\alpha$  radiation. Samples for clay mineralogy were first pre-

treated with 1.0 N ammonium acetate to remove any calcium carbonate and with 30 percent H<sub>2</sub>O<sub>2</sub> to remove most organic matter. The samples were then centrifuged to separate the silt and clay fractions. Preferred orientation of c-axes of the clay minerals perpendicular to the glass slide was obtained by pipetting a thick slurry of clay and distilled water onto a glass slide, allowing the clay minerals to settle out with a preferred orientation, and removing the water by evaporation.

### RESULTS AND DISCUSSION

Results of analyses of whole-rock samples for organic matter and carbonate by loss on ignition and gross mineralogy by X-ray diffraction are given in table 1. The amount of organic matter in the samples, as measured by loss on ignition between 100 and 550° C, is fairly low, ranging from a minimum of 1.8 percent in a limestone pebble from the flat-lying conglomerate at locality FW6 (unit 2) to 8.5 percent in gray shale in unit 2 at locality FW5.

The amount of organic matter, as determined by loss on ignition, in the Ciniza Lake Beds varies slightly (fig. 1). At locality FW1 the structureless mudstone in the base of the lake beds (FW1-2a) contains 3.7 percent organic matter. It rises to 5.4 percent in the next two higher samples (FW1-2b and FW1-2c) from the lower part of the gray shale that constitutes the bulk of the lake beds. The amount of organic matter is somewhat higher in the overlying lake beds and reaches a maximum of 7.6 percent in the uppermost sample (FW1-2j) in the lake beds. The average amount of organic matter found in the ten samples from the lake beds at locality FW1 is 6.3 percent. Samples of the lake beds from two other localities (FW5-2 and FW6-3) had 8.5 percent and 5.8 percent organic matter, respectively. The average amount of organic matter in the 12 samples of the lake beds was 6.5 percent.

The amount of organic matter in the lake beds (average of 6.5 percent) is high compared to that usually found in fine-grain sediments. Gehman (1962) reports that the amount of organic matter in shales ranges from practically 0 to 40 percent, but that it averages 1.1 percent. The Pleistocene Rita Blanca Lake Beds of Texas contain only about 0.05 percent organic matter (Kirkland and Anderson 1969). It is also unusually higher than the amount of organic matter found in other fine-grained rocks in the Chinle Formation. At locality FW1 the structureless mudstone (FW1-3) that overlies the lake beds contains 3.8 percent organic matter. The structureless mudstone at locality FW8, which contains abundant leaves, contains 2.9 percent organic matter.

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TABLE 1

IGNITION LOSS AT 550° C., IGNITION LOSS AT 1000° C., AND QUALITATIVE ESTIMATES OF QUARTZ, CALCITE, DOLOMITE, AND CHLORITE BASED ON PEAK HEIGHT OF X-RAY DIFFRACTION TRACES  
 + + + + = very strong peak; + + + = strong peak; + + = moderate peak; + = weak peak; 0 = no peak above background. All estimates are relative to these samples only. See chapter 1, figures 4 and 17 for location of samples.

Sample (locality and unit)	Percent Ignition Loss 550° C.	Percent Ignition Loss 1000° C.	X-ray Quartz	X-ray Calcite	X-ray Dolomite	X-ray Chlorite (7 Å)	X-ray Chlorite (3.5 Å)
FW1-3	3.8	5.9	+	0	0	0	0
FW1-2j	7.6	6.5	++	0	0	+	+
FW1-2i	6.3	5.9	++	0	0	0	0
FW1-2h	6.0	6.1	++	0	0	+	0
FW1-2g	6.5	5.6	++	0	0	++	++
FW1-2f	6.7	5.5	++	0	0	+	0
FW1-2e	6.5	6.3	++	0	0	0	0
FW1-2d	6.4	6.3	++	0	0	+	+
FW1-2c	6.9	6.2	+	0	0	++	++
FW1-2b	5.4	5.8	+	0	0	+	+
FW1-2a	5.4	6.6	+	0	0	++	++
FW1-1	3.7	4.4	++++	0	0	++	++
FW5-2	8.5	6.6	+	0	0	0	0
FW6-2	1.8	72.4	++	+++	+	0	0
FW6-3	5.8	5.1	+++	0	0	0	+
FW8	2.9	8.8	++	++	0	+	+

The loss on ignition of the sediments from the modern Lago di Monterosi in Italy is about three times that of the lake bed samples for this report (Cowgill and Hutchinson 1970). In one core from Lago di Monterosi, loss on ignition averaged 16.77 percent; in a second core it averaged 17.91 percent. This contrasts greatly with the samples analyzed in this report which had an average loss of 6.5 percent.

The carbonate content of the samples was estimated by two methods: (1) by assuming that the loss on ignition between 550 and 1000° C is the result of CO<sub>2</sub> loss from carbonate, and (2) by dissolving the carbonate in the very dilute acid ammonium acetate. Both methods are subject to errors in samples with a high clay content. As discussed by Dean (1974), the ignition-loss method works best for samples that contain greater than 10 percent calcium carbonate and little

clay. Measurement of carbonate in amounts less than 10 percent yields accurate results only if the other minerals do not lose lattice water between 550 and 1000° C; this loss may be as much as 5 percent of clay samples. During an acid extraction some clay minerals and ions absorbed on clays and organic matter will be dissolved in addition to the carbonate even if a mild acid like ammonium acetate is used. Therefore, the 4–6 percent ignition loss between 550 and 1000° C (table 1) and ammonium-acetate-soluble fraction (table 2) obtained for most samples of the material analyzed here probably does not represent carbonate. This conclusion is supported by the fact that no carbonates were detected by X-ray diffraction analyses of these samples. The limestone pebble in sample FW6-2 contains 72 percent carbonate by loss on ignition, which is probably correct because of the high-carbonate, low-

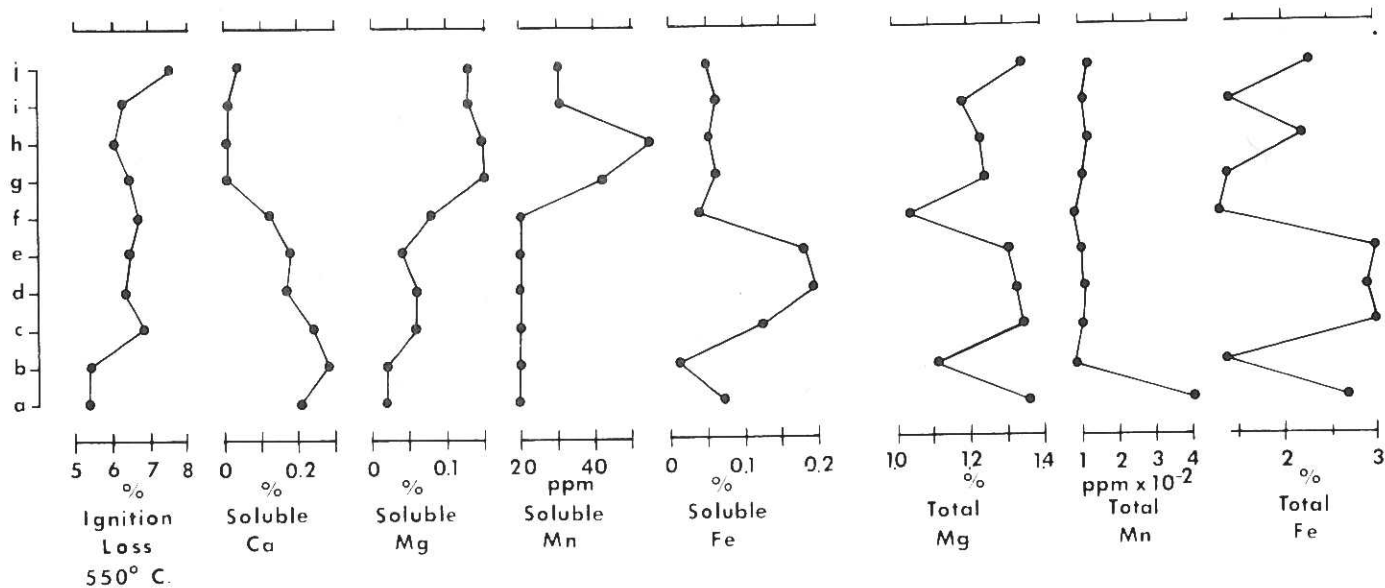


FIGURE 1.—Stratigraphic variations in ignition loss at 550° C, ammonium-acetate-soluble Ca, Mg, Fe, and Mn, and total Mg, Fe, and Mn in unit 2 of the lake beds at locality FW1.

TABLE 2

AMOUNT SOLUBLE IN 1.0 N AMMONIUM ACETATE, pH 5.2, CONCENTRATIONS OF CA, MG, FE, AND MN IN AMMONIUM ACETATE LEACHATE, AND TOTAL CONCENTRATIONS OF MG, FE, AND MN IN 16 SAMPLES.

All values expressed as percent or parts per million (ppm) dry weight of sample. See chapter 1, figures 4 and 17 for location of samples.

Sample (locality and unit)	NH <sub>4</sub> Ac Soluble (%)	Soluble Ca (%)	Soluble Mg (%)	Soluble Fe (ppm)	Soluble Mn (ppm)	Total Mg (%)	Total Fe (%)	Total Mn (ppm)
FW1-3	6.6	0.15	0.15	50	20	1.57	3.8	128
FW1-2j	5.6	0.04	0.13	500	30	1.35	2.3	124
FW1-2i	6.2	0.01	0.13	610	30	1.18	1.4	110
FW1-2h	4.5	0.01	0.15	560	55	1.24	2.2	126
FW1-2g	5.1	0.01	0.15	640	42	1.25	1.4	104
FW1-2f	4.8	0.13	0.08	410	< 20	1.04	1.3	96
FW1-2e	5.5	0.18	0.04	1850	< 20	1.31	3.0	100
FW1-2d	5.7	0.17	0.06	1950	< 20	1.33	2.9	101
FW1-2c	6.1	0.24	0.06	1290	< 20	1.35	3.0	104
FW1-2b	6.4	0.28	0.02	120	< 20	1.11	1.4	83
FW1-2a	5.5	0.21	0.02	710	< 20	1.36	2.7	405
FW1-1	7.1	0.86	0.03	230	322	8.9	1.2	2300
FW5-2	7.3	0.43	0.06	600	< 20	1.21	2.3	80
FW6-2	78.4	22.5	0.80	620	5600	1.79	0.3	7900
FW6-3	4.7	0.02	0.14	500	30	1.18	1.6	111
FW8	8.6	2.57	0.45	260	510	1.50	1.9	860

clay content of the sample. X-ray diffraction results also show calcite in the gray shale at section FW6. Therefore, ignition loss and acid solution of this sample would represent some carbonate, but probably somewhat less than the 8.8 percent indicated by ignition loss and the 8.6 percent indicated by acid solution.

In general, there is very little variation in gross mineralogy (table 1), and most X-ray diffractograms of randomly oriented, untreated samples are dominated by peaks for quartz, and to a lesser extent by peaks for chlorite. As mentioned above, the limestone pebble in sample FW6-2 and the gray mudstone at locality FW8 were the only samples which contained measurable amounts of carbonate. The only dolomite detected was in the limestone pebble in sample FW6-2. Although gypsum did not appear in any of the X-ray diffraction patterns, some gypsum does occur as fracture filling, particularly in sample FW6-3. This gypsum probably precipitated from sulfate-rich groundwaters and is therefore much younger than the deposits in which it occurs.

Results of X-ray diffraction analyses of the clay-size ( $2\mu$ ) fraction from the 16 samples are presented in table 3. Typical X-ray diffraction patterns of clay-size material are shown in figure 2. Most diffractograms are characterized by a dominant quartz peak at 3.35 Å. This peak overlaps with the 3.36 Å mica peak, but judging from the intensities of the 4.3 Å and 3.35 Å quartz peaks, quartz is by far the dominant contributor to the 3.35 Å peak. Usually, the second most dominant peak is at 7 Å because of kaolinite and chlorite. Most diffraction patterns of clay samples also show a small 10 Å mica (illite) peak and a broad peak between 11 and 12 Å resulting from mixed-layer clays, probably an interlayering of illite and montmorillonite. Additional mica peaks occur at 10 Å, 5 Å, and 4.5 Å, and probably overlapping the dominant quartz peak at 3.3 Å.

Schultz (1963) reported that illite and mixed-layer illite-montmorillonite are the dominant clay minerals in the Chinle Formation at a nearby locality at the same approximate horizon as the lake beds. In contrast, the clay miner-

TABLE 3

QUALITATIVE ESTIMATES OF MICA, KAOLINITE + CHLORITE, QUARTZ, FELDSPAR, AND MICA X-RAY DIFFRACTION PEAK HEIGHTS FROM CLAY-SIZE ( $< 2\mu$ ) FRACTIONS.

++ = very well-defined peak; + = well-defined peak; tr = poorly defined peak; 0 = no peak above background. All estimates are relative to these samples only. See chapter 1, figures 4 and 17, for location of samples.

Sample (Sect.-Unit)	Mica (10 Å)	Kaolinite + chlorite (7 Å)	Quartz + mica (3.35 Å)	Feldspar (3.2 Å)	Mixed layer mica (11-12 Å)	Mica (4.5 Å)
FW1-3	tr	tr	++	0	broad	+
FW1-2j	nd	nd	nd	nd	nd	nd
FW1-2i	+	+	++	0	broad	tr
FW1-2h	tr	+	++	0	broad	tr
FW1-2g	tr	+	++	0	broad	tr
FW1-2f	+	++	++	0	broad	tr
FW1-2e	tr	+	++	0	broad	tr
FW1-2d	+	++	++	tr	broad	tr
FW1-2c	tr	++	++	tr	broad	tr
FW1-2b	tr	++	+	0	broad	0
FW1-2a	+	++	+	0	broad	tr
FW1-1	tr	++	++	0	0	tr
FW5-2	tr	+	++	tr	broad	+
FW6-2	0	tr	++	0	0	tr
FW6-3	+	+	++	0	broad	+
FW8	tr	tr	++	0	0	+

alogy of the lake beds is dominated by kaolinite (and possibly chlorite) and the illite-mixed-layer assemblage. These differences, however, are not too significant as they probably reflect the environment of deposition of the clay minerals. Presumably the clays were altered to a greater extent in the lake than in the fluvial environment in which the more typical Chinle sediments analyzed by Schultz were deposited. Thus there would be a considerable amount of mixed layering in the lake clays, and the differences are simply differences in the mixture of them.

The clay minerals in the Ciniza Lake Beds do not give clues as to whether the beds are definitely lacustrine or fluvial as the minerals found could occur in either environment. Weaver (1958) showed that the major clay minerals can occur in abundance in any major depositional environment. None of the clay mineral assemblages (e.g., attapulgite-sepiolite) associated presently with alkaline carbonate desert lakes occur in the lake beds.

Results of atomic absorption analyses of ammonium-acetate-extractable Ca, Mg, Fe, and Mn, and total Mg, Fe,

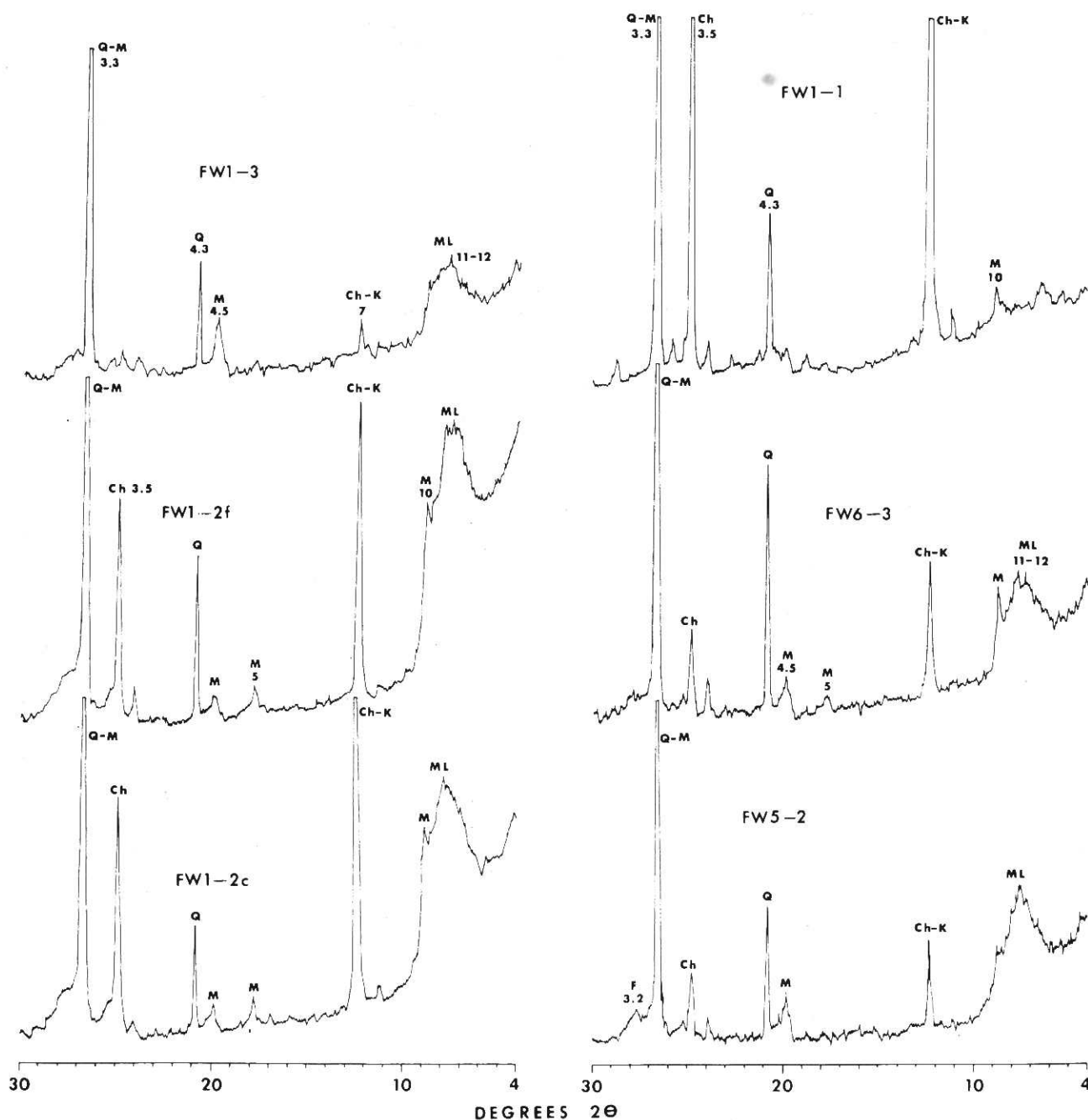


FIGURE 2.—Representative X-ray diffraction traces of clay-size (<2 $\mu$ ) fractions from the Ciniza Lake Beds and associated rocks. M—mica; Q—quartz; Ch—chlorite; K—kaolinite; ML—mixed-layer mica; F—feldspar; numbers above peaks refer to d-spacings in Ångström units, Å.

TABLE 4

COMPARISONS OF CONCENTRATIONS OF CA, MG, FE, AND MN IN AMMONIUM ACETATE LEACHATES FROM SEDIMENTS FROM 20 NONCARBONATE MINNESOTA LAKES, AND TOTAL CONCENTRATIONS OF MG, FE, AND MN IN SEDIMENTS FROM 20 NONCARBONATE MINNESOTA LAKES, 15 MARINE SHALES, AND 15 FRESHWATER SHALES WITH SIMILAR DATA FROM THE LAKE BEDS (SAMPLES FW1-2A-2J) AND CLAYSTONE IN THE MAIN BODY OF THE MONITOR BUTTE MEMBER OF THE CHINLE FORMATION (SAMPLES FW1-3 AND FW8). Data for the Minnesota lakes are from Dean and Gorham (1976), and those for the marine and freshwater shales are from Keith and Degens (1959).

Sample	Soluble Ca (%)	Soluble Mg (%)	Soluble Fe (ppm)	Soluble Mn (ppm)	Total Mg (%)	Total Fe (%)	Total Mn (ppm)
Minnesota Lakes	0.5-1.0	0.05-0.15	100-3000	100-2500	0.3-0.9	2-8	500-2800
Marine Shales					1.12 ± 0.17	6.67 ± 3.34	800 ± 500
Freshwater Shales					1.04 ± 0.09	5.82 ± 2.13	1200 ± 700
Lake Ciniza Beds	0.01-0.28	0.02-0.15	120-1950	< 20-50	120 ± 0.16	2.1 ± 0.9	24 ± 162
Chinle Claystone	0.15-2.57	0.15-0.45	50-260	20-510	1.54 ± 4	2.8 ± 1.0	494 ± 366

and Mn are given in table 2. Stratigraphic variations of these elements in samples from locality FW2 in unit 2 are shown in figure 1. Most ammonium-acetate-soluble Ca is probably derived from dissolution of calcite. The low concentrations of acid-soluble Mg, Fe, and Mn, relative to the total amounts present, suggest that most of these elements are in clay mineral lattice sites or are present as ammonium-acetate-insoluble oxides or sulfides. The relatively high acid soluble Mg (0.8 percent) and Mn (0.56 percent) in the limestone pebble from unit 2 at locality FW6 indicate that these elements are associated with calcite, presumably in solid solution with calcite because dolomite is not dissolved by ammonium acetate.

Table 4 shows the ranges of total Fe, Mg, and Mn in sediments from 20 noncarbonate Minnesota lakes and 30 marine and nonmarine shales. From their study of trace and minor elements in 15 marine and 15 nonmarine shales (as indicated by well-documented fossil evidence), Keith and Degens (1959) concluded that concentrations of most trace major and minor elements were not significantly different in shales from the two environments. However, they did find significant differences for S, Li, B, and Ga. The Mg concentrations in the Ciniza Lake Beds are relatively constant at 1.2 to 1.4 percent dry weight, slightly higher than the Minnesota lake sediments, the marine shales, or the nonmarine shales (table 4). Concentrations of both Fe and Mn are less than those given in table 4 and show little variation between samples.

None of the minor element concentration ranges in table 2 show any unusual values which might be useful in providing conclusive evidence regarding the origin of the Ciniza Lake Beds. The lower concentrations of Fe than would normally be expected in either marine or nonmarine shales would tend to suggest a freshwater rather than a marine origin, but this evidence is very weak.

#### CONCLUSIONS

1. The Ciniza Lake Beds consist predominately of low carbonate shale composed chiefly of quartz, mica, and clays.

2. Clay minerals in the Ciniza Lake Beds are predominately kaolinite + chlorite (7 and 3.5 Å), mica (mostly 10 Å illite), and mixed-layer illite and montmorillonite (broad 11-12 Å peak).

3. The Ciniza Lake Beds contain a large amount of organic matter in comparison to the average shales.

4. The concentration of Mg is higher, and the concentrations of Fe and Mn are lower than one might expect to find in either marine or nonmarine shales.

5. The mineralogical and minor element data yield no clear suggestion about the environment in which the Ciniza Lake Beds accumulated.

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