

HAMYROLYSIS OF ILLITE AND MONTMORILLONITE
AN EXPERIMENTAL INVESTIGATION

HAMYROLYSIS OF ILLITE AND MONTMORILLONITE:

AN EXPERIMENTAL INVESTIGATION

by

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TABLE OF CONTENTS

Acknowledgements	iii
Abstract	iv
List of Tables and Figures	v
Introduction	1
Experimental	5
Materials	8
Results: Water Analysis	13
Cation Exchange Experiments	21
X-Ray Diffraction	23
Conclusions	29
Discussion	30
Appendix I	41
Appendix II	42
References	44

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ABSTRACT

The short term (5000 hours) stability of illite and montmorillonite in sea water was studied by suspending 5.00 gm. aliquots of A.P.I. reference clays Montmorillonite # 25b and Illite # 35 in 500 ml. of artificial sea water (tradename "Instant Ocean"). After 5000 hours, in the montmorillonite samples, Ca and Si concentrations had increased (0.490 mmol/L and 0.289 mmol/L respectively), the cation exchange capacity had decreased (104.36 meq/100 gms. to 81.42 meq/100 gms.), the pH had decreased (8.40 to 7.94) but no major mineralogical change was observed. After 5000 hours, in the illite samples, Si concentration had increased (0.045 mmol/L), the cation exchange capacity remained the same, the pH increased (7.22 to 7.60) and no major mineralogical change was observed. The release of Ca in the illite samples was complicated by the dissolution of calcite and significant changes in concentration of other cations (Na, K, Mg) were not observed.

The data for Si, cation exchange and exchangeable cations are compared to that of Lewis (1950), Whitehouse and McCarter (1956), Carrol and Starkey (1958), MacKenzie et al (1965) (1967) and Russell (1970), a model developed by Houston (1972) is used to explain the Ca and Si data for the montmorillonite samples, and the implications of the apparent stability of these minerals to the case for authigenic clay formation from detrital material are discussed.

LIST OF TABLES AND FIGURES

Table I	Percentages of Total Clay Fraction for Illite and Montmorillonite in sediments from the world's oceans.
Table II	Time Intervals and Types of Analysis at each Interval.
Table III	Composition of Artificial Seawater.
Table IV	(a) Change in Element Concentration of Supernatant Water with time Montmorillonite. (b) Change in Element Concentration of Supernatant Water with time Illite.
Table V	Total Alkalinity of Supernatant water after 5000 hours.
Table VI	Degree of Calcite Saturation for samples.
Table VII	Cation exchange capacity and exchangeable cations.
Table VIII	Comparison of Elemental Ratios of exchangeable cations.

Figure I

- (a) Unoriented X-Ray diffraction pattern
Illite # 35.
- (b) Unoriented X-Ray diffraction pattern
Montmorillonite # 25b.

Figure II

- (a) Change in Si (i.e. Δ Si) concentration
with time.
- (b) Change in Ca (i.e. Δ Ca) concentration
with time.
- (c) Change in pH (i.e. Δ pH) concentration
with time.
- (d) pH with time.

Figure III

Oriented X-Ray diffraction pattern Illite

Figure IV

- (a) Oriented X-Ray diffraction pattern
Montmorillonite (Moist)
- (b) Oriented X-Ray diffraction pattern
Montmorillonite (150°)
- (c) Oriented X-Ray diffraction pattern
Montmorillonite (Glycolated)
- (d) Oriented X-Ray diffraction pattern
Montmorillonite (450°)

Figure V

General form of concentration vs time curves

- (a) no saturation
- (b) saturation

Figure VI

Form of curves for adsorption and dissolution

(a) adsorption

(b) dissolution

Figure VII

Silica concentration as a function of time ---

Figure VIII

Stability diagram for Montmorillonite/Illite
solid solution series.

INTRODUCTION

The processes responsible for the distribution of clay minerals in today's oceans have been a great controversy for at least the last fifty years. Some investigators propose that all clay minerals are detrital in origin and therefore dependent upon the nature of their source for their mineralogy. (Correns (1937), Weaver (1958), Griffin (1962), Biscaye (1965).) Others propose the authigenic formation of clays in transport and in situ. Dietz (1941), Powers (1954), Johns et al (1958), Peterson et al (1964), MacKenzie (1966) and Jeans (1971).

Correns (1937) found no evidence for diagenetic change in clay mineralogy in cores taken from the Meteor. Dietz (1941) found evidence for the development of illite in Recent sediment samples taken from Challenger. Bradley (1945) introduced glycolation techniques in X-ray diffraction which made possible more precise identification of clay minerals.

Over the years many authors have shown from experimental and field studies that authigenic formation of clay minerals is possible and occurs in Recent sediments. Whitehouse and McCarter (1956) observed diagenetic changes in montmorillonite initiated by flocculation in artificial sea water with Chlorinities ranging from 8-10 ppt. After 60 months, they separated by gravity settling four fractions which were identified as montmorillonitic, chloritic, illitic and unidentified. They also found that absorption of the carbohydrates raffinose and fucocdin by montmorillonite caused the clay to preferentially absorb K and had not undergone major alteration at the end of 60 months. Whitehouse et al's study has been criticized by Berner (1971) because they didn't similarly fractionate the initial reactant mineral and by Perry (1971) for not looking for vermiculite.

Russell (1970) found that natural samples of clay from the Rio Ameca River high in montmorillonite absorbed Mg^{++} preferentially during laboratory exposure to sea water but no changes in mineralogy were noted. Marine clays in the same area did not show preferential absorption of Mg^{++} .

Authigenic formation of clay minerals has been defined in field studies of Recent sediments. Peterson et al (1964) showed that the authigenic formation of montmorillonite from volcanic glass in the South Pacific. Powers (1957) showed the rapid formation of a chlorite-like clay from montmorillonite and weathered illite through a mixed layered illite-vermiculite-chlorite in Chesapeake Bay. Johns and Grim (1958) showed that the average montmorillonite content of Mississippi River water decreased slightly but abruptly upon contact with saline water. They attributed this to the reconstitution of degraded illite and chlorite. They found montmorillonite continued to fix both K and Mg to form illite and chlorite.

Weaver (1958) contends that montmorillonite formed from mica will readily absorb K from sea water and form illite but that montmorillonite formed from volcanic glass would not likely alter to 10\AA illite. However he states that most marine sedimentary montmorillonites are not pure but contain 10-30% intergrown contracted 10\AA illite.

In contrast to Johns and Grims (1958) paper on the Gulf of Mexico sediments, Griffin (1962) attributed the distribution of clay minerals to detrital processes and the type of clay which predominated in the drainage basins of the rivers emptying into the Gulf of Mexico. There have been proponents of authigenic formation of clays from gels of Al, Fe and Si. (McKenzie et al (1966), Jeans (1971). McKenzie estimates that authigenic clays comprise only 7% of all clay minerals in the oceans but that this is enough to keep the ocean in a steady state with respect to Na^+ , K^+ , and Mg^{++} .

Authigenic formation of clay minerals only effects the distribution of clay minerals in areas of the ocean where detrital processes are not dominant and rates of sedimentation are low. Whether authigenic formation of clay minerals was instrumental in the evolution of the ocean or in the maintenance of its present state, is beyond the scope of this study.

The prime objective of this study is to establish the short range stability in sea water of illite and montmorillonite which make up a large percentage of the clays present in Recent marine sediments. Table I shows the percentages of the total clay fraction in ocean sediments which are illite and montmorillonite.

TABLE I

Percentages of total clay fraction for Illite and Montmorillonite in sediments from the world's oceans.

	Montmorillonite		Illite	
	<u>Number of Samples</u>	<u>%</u>	<u>Number of Samples</u>	<u>%</u>
North Atlantic	206	16	202	55
South Atlantic	214	26	208	47
North Pacific	170	35	170	40
South Pacific	145	53	146	26
Indian	129	41	129	33

from Griffin (1968)

EXPERIMENTAL

Experiments were designed to study the interaction of two clays illite and montmorillonite with artificial sea water and to determine their stability in an artificial ocean environment over a relatively short time interval (5000 hours).

Two A.P.I. reference clays were used, Illite # 35 and Montmorillonite # 25b. The clays were passed through a 200 mesh standard seive and duplicate 5000 gram aliquots of the seived clay were added to 500 ml. of artificial sea water in a 500 ml. polyethylene bottle which was capped and placed on a shaker table with two bottles of artificial sea water to act as control samples. The samples were shaken for 1500 hours at which time they were removed from the shaker table and allowed to stand for the next 3500 hours. The samples were kept at room temperature during the entire experiment. Aliquots of the suspension were taken at the intervals shown in Table II and the analysis shown also in Table II were performed on the supernatant water. The aliquots were taken while the sample was being vigourously stirred in order to obtain a homogeneous suspension. The pH of the sample was measured in the bottle before taking an aliquot at each interval.

Before the 100 hour interval, the clay was allowed to settle under gravity before analysis. Fine particles of clay caused difficulties in the analysis, so at all intervals after 100 hours and including 100 hours, the samples were centrifuged and the supernatant water separated by pipet before analysis.

Atomic absorption was used to analyse for all elements before the 5000 hour interval. A 1000 ppm silicon standard was prepared according to Buckley and Cranston (1971) and then diluted to 10 ppm with artificial sea water.

TABLE II

Time intervals and types of analysis.

<u>Time Element</u> <u>(Hours)</u>	<u>Sample</u> <u>Centifuged</u>	<u>Na</u>	<u>K</u>	<u>Ca</u>	<u>Mg</u>	<u>Sr</u>	<u>Li</u>	<u>pH</u>	<u>Si</u>	<u>Si</u> (Govett)
1	NO	✓	✓	✓	✓	✓	✓	✓	✓	
25	NO	✓	✓	✓	✓	✓	✓	✓	✓	
50	NO	✓	✓	✓	✓	✓	✓	✓	✓	
100	YES	✓	✓	✓	✓	✓	✓	✓	✓	
200	YES	✓	✓	✓	✓	✓	✓	✓	✓	
500	YES	✓	✓	✓	✓	✓	✓	✓	✓	
5000	YES	✓	✓	✓	✓			✓		✓

At 5000 hours, the elements Na, K, Ca and Mg were analysed by atomic absorption using an artificial sea water standard. Silica was analysed according to a spectrophotometric method adapted from Govett (1961) for use in saline waters by using standards made by dilution of a 1000 ppm SiO_2 solution with the artificial sea water used as an atomic absorption standard mentioned above. Also at 5000 hours the total alkalinity of the supernatant water was measured according to Strickland and Parsons (1961).

The cation exchange capacity of the clays and the exchangeable cations were determined for samples exposed to artificial sea water for 1 hour and 5000 hours. The procedure used was adapted from Russell (1970). Five mls. of homogeneous clay suspension were filtered through a 10m μ Millipore filter and then washed with deionized water until the filtrate gave a negative AgNO_3 test. The samples were then washed four times with 5 ml. of 1N NH_4Cl adjusted to pH 7 with NH_4OH and then with 5 ml. of deionized water to make 25 ml of filtrate. The filtrate was analysed by atomic absorption of K and Na and by atomic emission for Ca and Mg.

To determine the exact amount of clay used in the cation exchange experiments, five mls, of the same suspension was allowed to dry on tared watch glasses and the weight of clay determined by difference corrected for weight of sea water salts.

The clays both reacted and unreacted were subjected to X-ray diffraction analysis using Cu K_α Ni filtered radiation, a 1° divergence slit and a chart speed of $2^\circ \ 2\theta/\text{min.}$ under the following conditions:

(I) Oriented slides were made of washed clays by pipeting the clay suspensions onto a glass slide and allowing to dry at low heat on a hot plate. The X-ray diffraction analysis was done on the clays while they were still moist.

(II) The slides of the clay samples were dried at 150° C overnight and X-rayed again.

(III) The clays were saturated with ethylene glycol by placing in an oven in a closed container at 60° C for one hour. They were then X-rayed a third time.

(IV) The clay samples were heated to 450° C for approximately four hours and then X-rayed.

Materials

Illite # 35 - This clay was obtained from an outcrop south of Fithian, Illinois. The illite is the underclay of an 18 in. coal seam and below it, the clay suddenly changes to a calcareous facies which grades into an underlying sandstone. The illite sampled is the purest clay of the 6 foot underclay outcrop. Main (1950) performed a microscopic examination of the clay and found approximately 12% impurities. The impurities are distributed as follows: sericite 5%; quartz 2%; plagioclase 2%; pyrite 2%; calcite 1% with a trace of carbonaceous inclusions. An unoriented X-ray diffraction pattern is shown in Figure I (a).

Montmorillonite # 25b - This clay was obtained from a bentonite outcrop northeast of Newcastle, Wyoming. The clays are interbedded with sandstone and shales. The bottom contact is usually sharp and the underlying few inches of shale is extremely hard due to the addition of leached silica from the volcanic ash. This clay exhibited no fragmental volcanic material in thin section (Main 1950). The clay has 12% impurities distributed as follows: quartz 5%, sodic plagioclase 3%, orthoclase 2%, calcite 0.5%. The calcite is a secondary replacement of montmorillonite.

"The clay is doubtless of volcanic origin, but it has possibly been moved on more than one occasion and may have participated in a sedimentary series more than once after erosional intervals" (Main 1950). An unoriented X-ray diffraction pattern for Montmorillonite 25b is shown in Figure I (b).

Artificial sea water was used to eliminate any possible complications from organic or biological interactions with the clays. The artificial sea water used was a commercial preparation used in sea water aquaria (Instant Ocean).

Table III shows the artificial sea water's composition and compares the ratios of cation to sodium concentrations for the artificial sea water, as stipulated by the manufacturer and for mean ocean water. Although the artificial sea water used was less saline than average sea water, the cations are present in approximately the same proportions as in natural sea water.

UNORIENTED X-RAY DIFFRACTION PATTERN FOR ILLITE #35

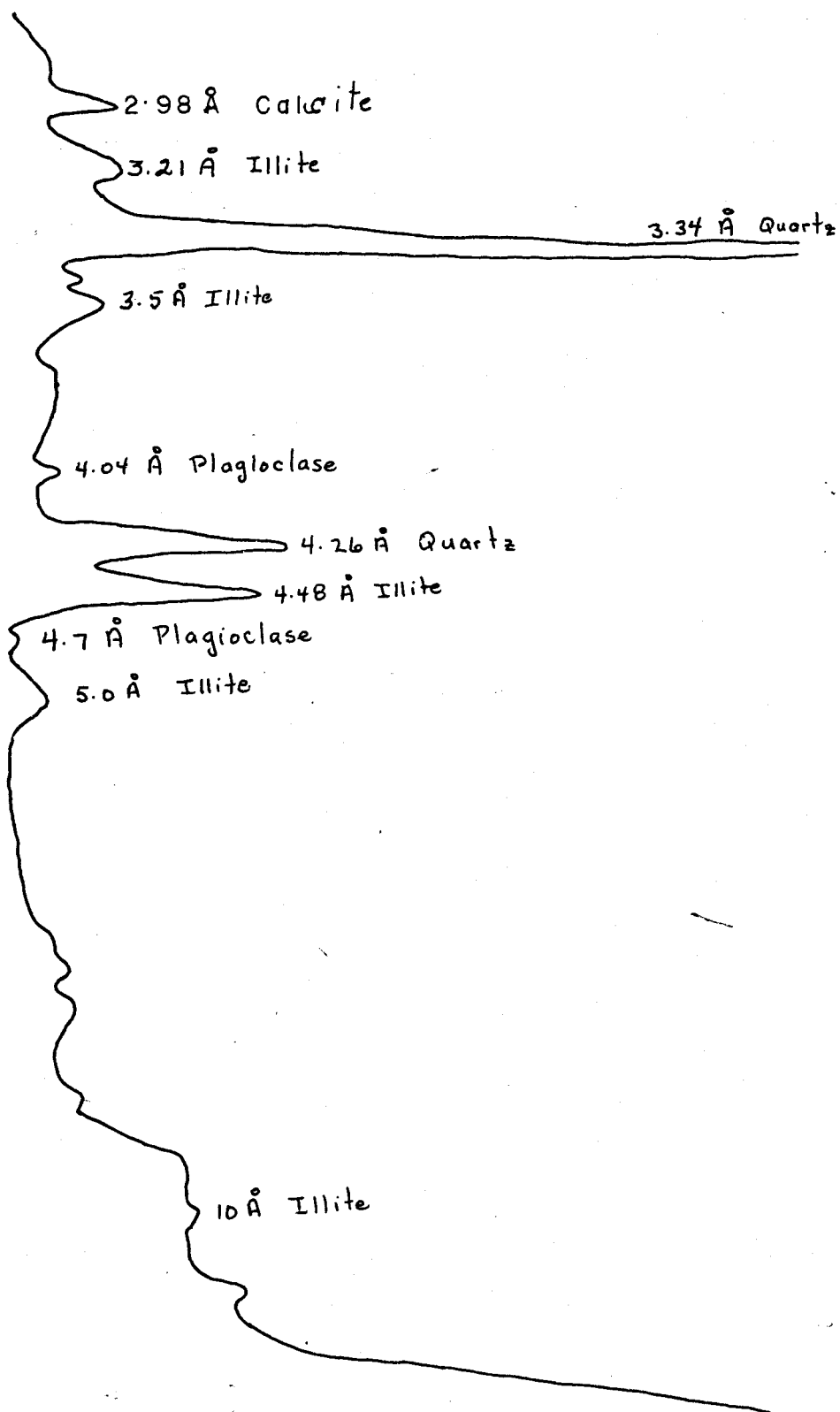


FIGURE I(b)

UNORIENTED X-RAY DIFFRACTION PATTERN FOR MONTMORILLONITE #25b

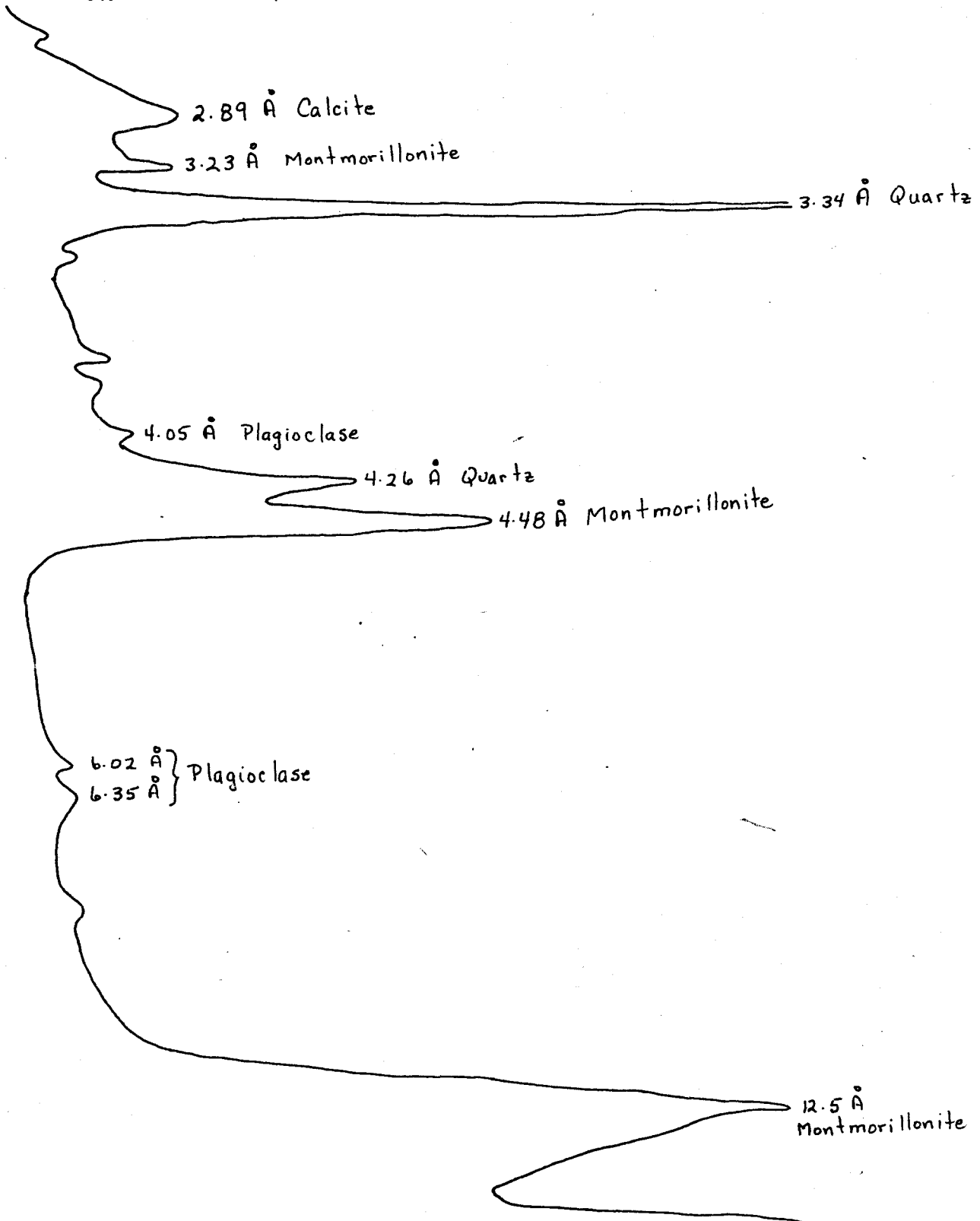


TABLE III

Composition of artificial seawater and elemental ratios
for artificial seawater, "Instant Ocean", and natural seawater.

<u>Element</u>	<u>Artificial Seawater</u>		<u>"Instant Ocean"</u>	<u>Mean Seawater*</u>	
	Conc. (ppm)	$\frac{[X]}{[Na]}$	$\frac{[X]}{[Na]}$	Conc. (ppm)	$\frac{[X]}{[Na]}$
Na	8203.	1.0	1.0	10,556.	1.0
K	322.6	0.039	0.036	380.	0.036
Mg	899.6	0.110	0.118	1,272.	0.120
Ca	298.3	0.036	0.036	400.	0.038

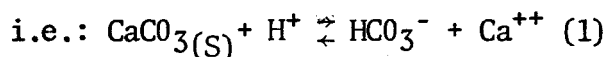
* from Krauskopf (1967)

Results: Water Analysis

Significant changes in concentration were only seen for Ca, Si, and pH. The analytical method was not sensitive enough to detect the small concentration changes of other elements. The change in element concentration was calculated by subtracting the mean concentration for the controls from the concentration of the samples. These data are given for Ca, Si, and pH for each time interval in Tables IV (a) and IV (b) and are shown graphically in Figures II (a), II (b), II (c) and II (d).

The silica concentration for the montmorillonites shows an initial very high concentration (Figure II (a)) which reduces to a much lower value then slowly begins to increase again. The same trend is shown in the illite silica data (Figure II (a)) at lower concentrations except that the silica concentration levels out after the initial "peak" and does not increase again. This initial "peaking", also seen in the Ca data (Figure II (b)) is attributable to initial hydration of the mineral surface (Houston 1972).

The illites apparently released more Ca than did the montmorillonites (see Figure II (b)). Because of the presence of calcite in the clays (see Materials) it was necessary to confirm that the Ca was actually from the clays and not the dissolution of CaCO_3 . Table V shows the total alkalinity of the supernatant water after 5000 hours. If calcite had been dissolving, an increase in total alkalinity over the control samples would be expected and also an increase in pH.



Both the montmorillonite and illite samples show a decrease in total alkalinity. The pH trends (Figure II (d)) of the montmorillonite further dispute the possibility of calcite dissolution but the illite pH trend

TABLE IV (a)

Change in element concentration of supernatant water with time
for Montmorillonite

Montmorillonite (#13)

Change in Element Conc. (mmoles/l)	Time (hours)						
	1	25	50	100	192.5	571.3	4704
ΔSi	-	-	+0.266	+0.138	+0.119	+0.114	+0.284
ΔCa	+0.349	-0.04	+0.169	+0.016	+0.158	+0.41	+0.515
ΔpH	-0.25	-0.31	-0.32	-0.32	-0.30	-0.28	-0.03
pH	8.39	8.35	8.31	8.21	8.18	7.78	7.94

Montmorillonite (#14)

ΔSi	-	-	+0.275	+0.140	+0.149	+0.122	+0.294
ΔCa	+0.449	-0.208	+0.124	+0.165	+0.158	+0.55	+0.465
ΔpH	-0.24	-0.30	-0.31	-0.32	-0.29	-0.06	-0.02
pH	8.40	8.36	8.32	8.21	8.19	8.00	7.95

NOTE: $\Delta X = [X]_{\text{sample}} - [X]_{\text{Control Mean}}$

ΔpH and pH in pH units

TABLE IV (b)

Change in element concentration of supernatant water with time
for Illite.

Illite (#11)

Change in Element Conc. (mmoles/l)	Time (hours)						
	1	25	50	100	192.5	571.3	4704
Δ Si	-	-	+0.423	+0.058	+0.039	+0.051	+0.043
Δ Ca	+1.55	+0.458	+0.855	+0.859	+0.926	+1.08	+1.22
Δ pH	-1.42	-1.40	-1.19	-1.00	-0.81	-0.84	-0.33
pH	7.22	7.26	7.44	7.53	7.67	7.22	7.64

Illite (#12)

Δ Si	-	+0.123	+0.115	+0.117	+0.054	+0.055	+0.047
Δ Ca	+0.449	-0.208	+0.833	+0.617	+0.881	+1.22	+1.09
Δ pH	-1.48	-1.43	-1.19	-1.04	-0.87	-0.80	-0.40
pH	7.16	7.23	7.44	7.49	7.61	7.26	7.57

NOTES: $\Delta X = [X]_{\text{sample}} - [X]_{\text{Control Mean}}$

Δ pH and pH are in pH units

FIGURE II (a)

CHANGE IN CONCENTRATION OF Si WITH TIME

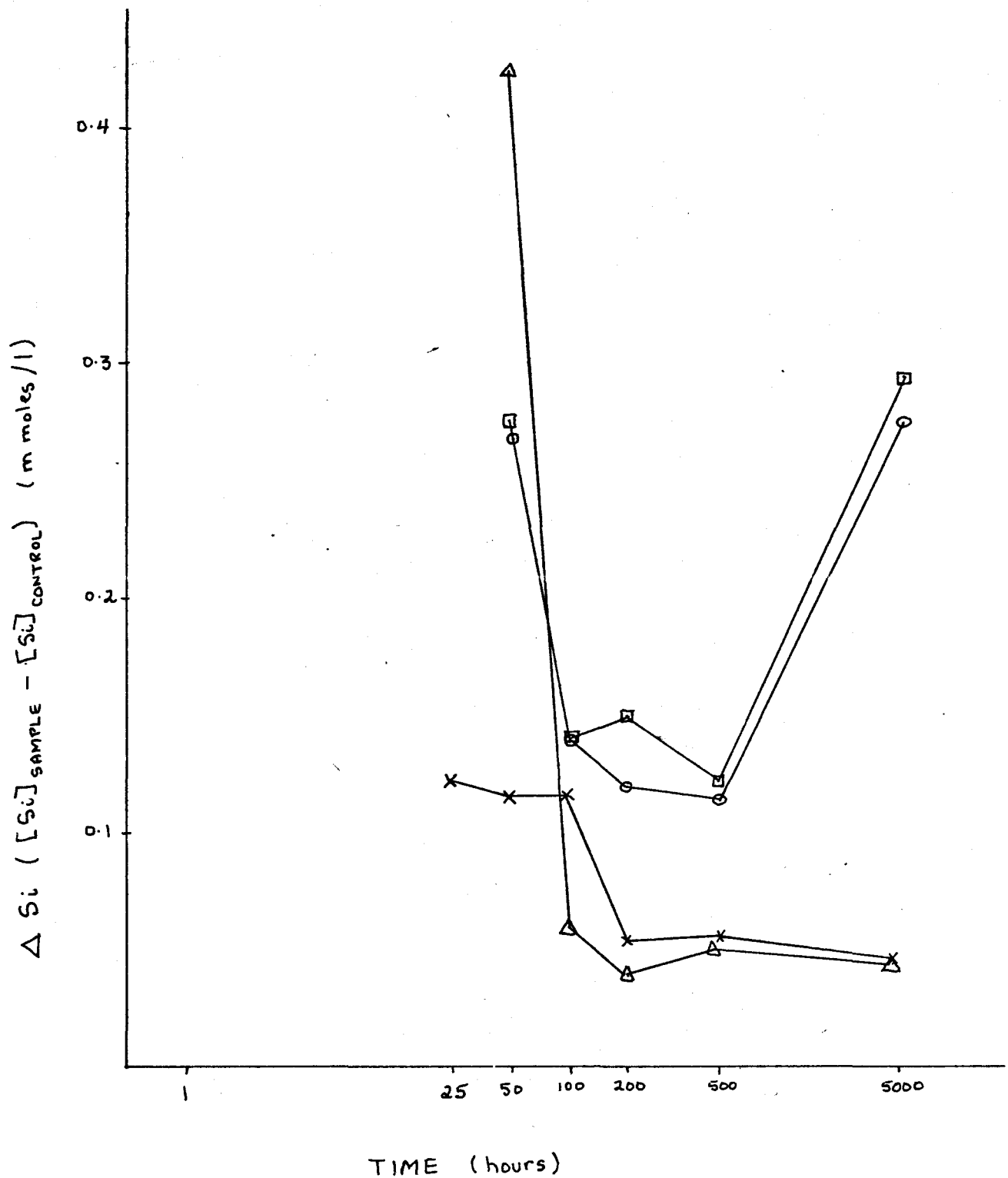


Figure II(a)

○ MONTMORILLONITE #13
 □ MONTMORILLONITE #14

Δ ILLITE #11
 X ILLITE #12

} DUPLICATE SAMPLES

CHANGE IN CONCENTRATION OF Ca WITH TIME

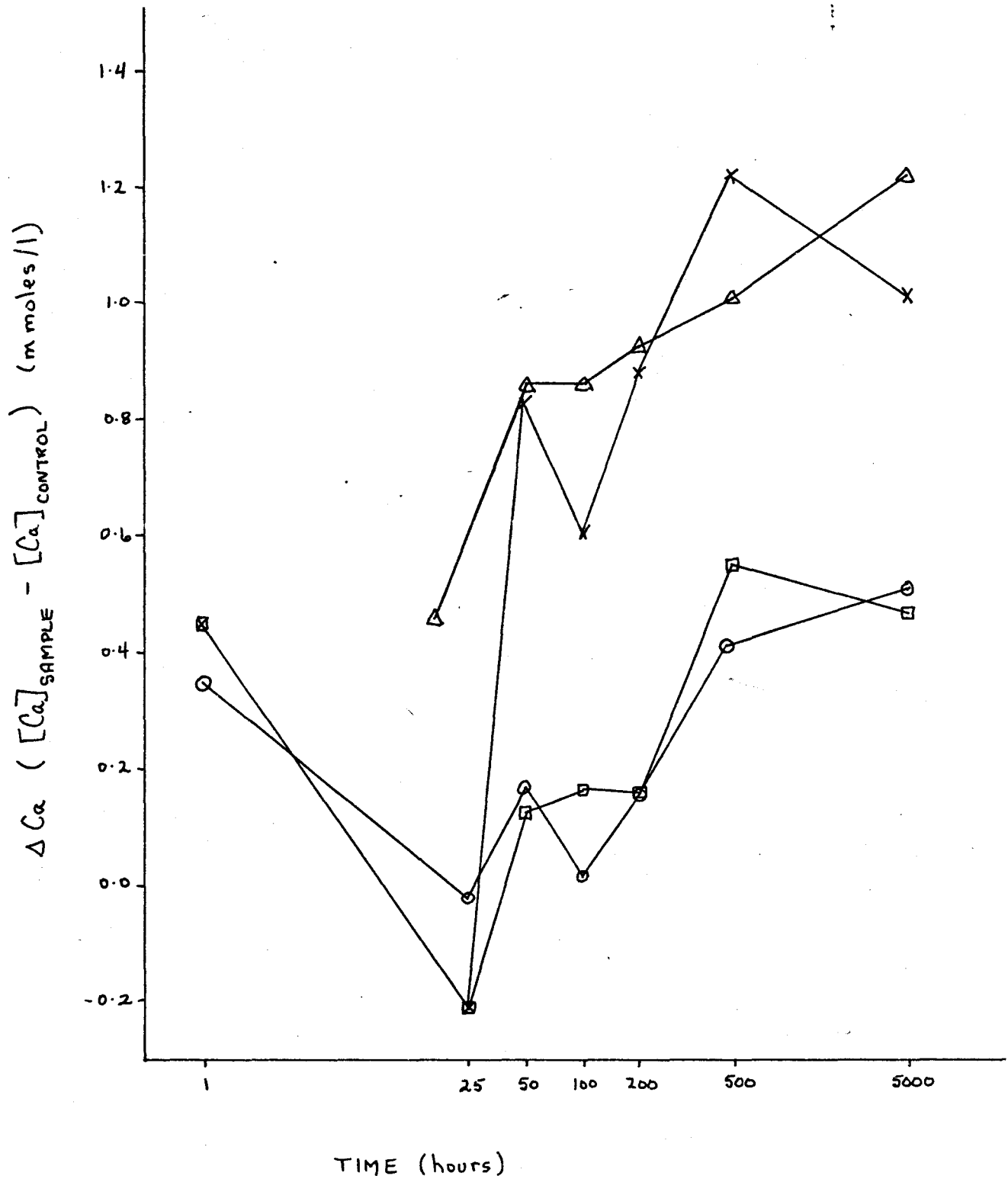


Figure II (b) for explanation of symbols see Figure II(a)

FIGURE II (c)

CHANGE IN DELTA PH WITH TIME

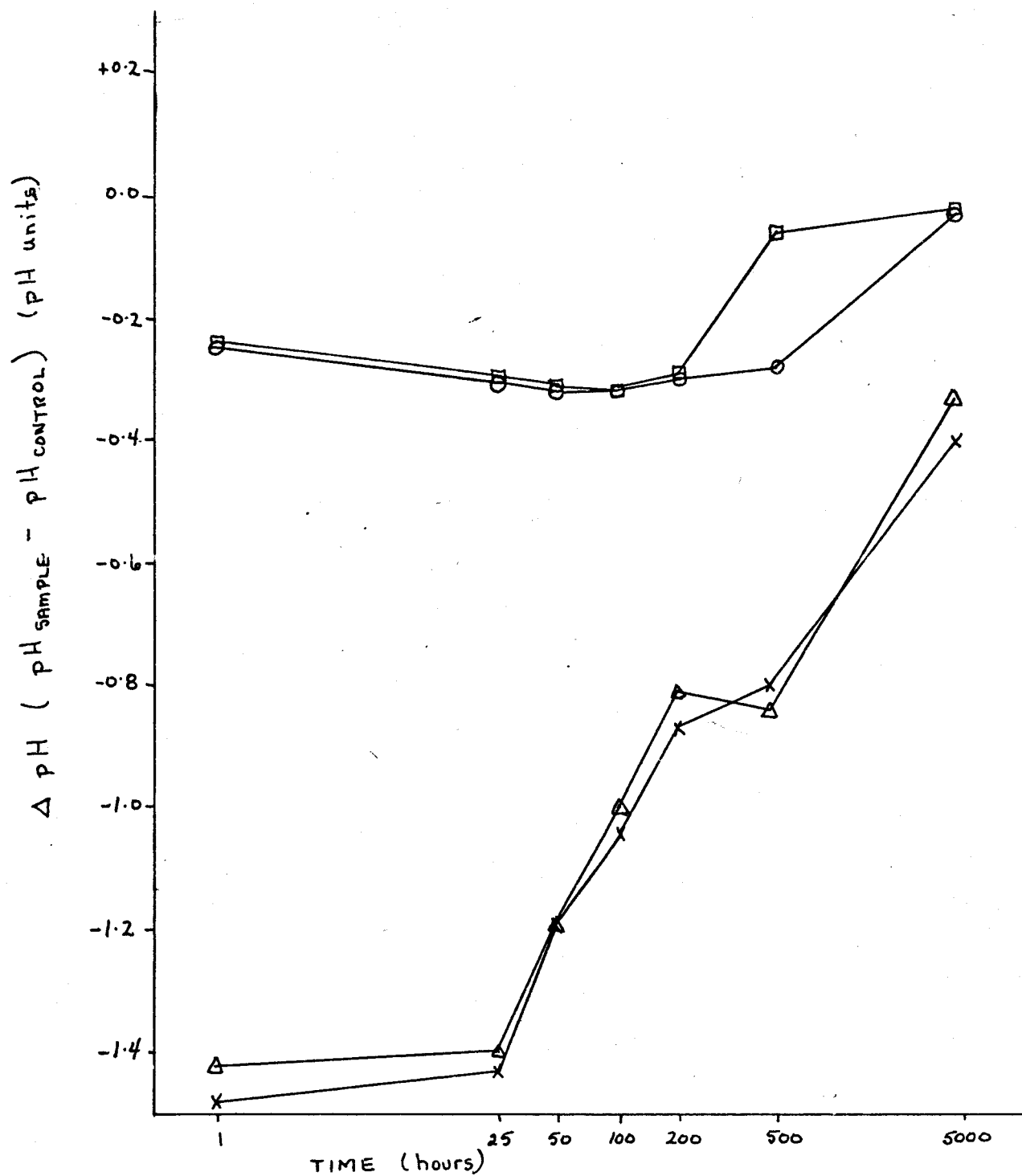


Figure II (c) See FIGURE II (a) for explanation of symbols

FIGURE II (d)

CHANGE IN PH WITH TIME

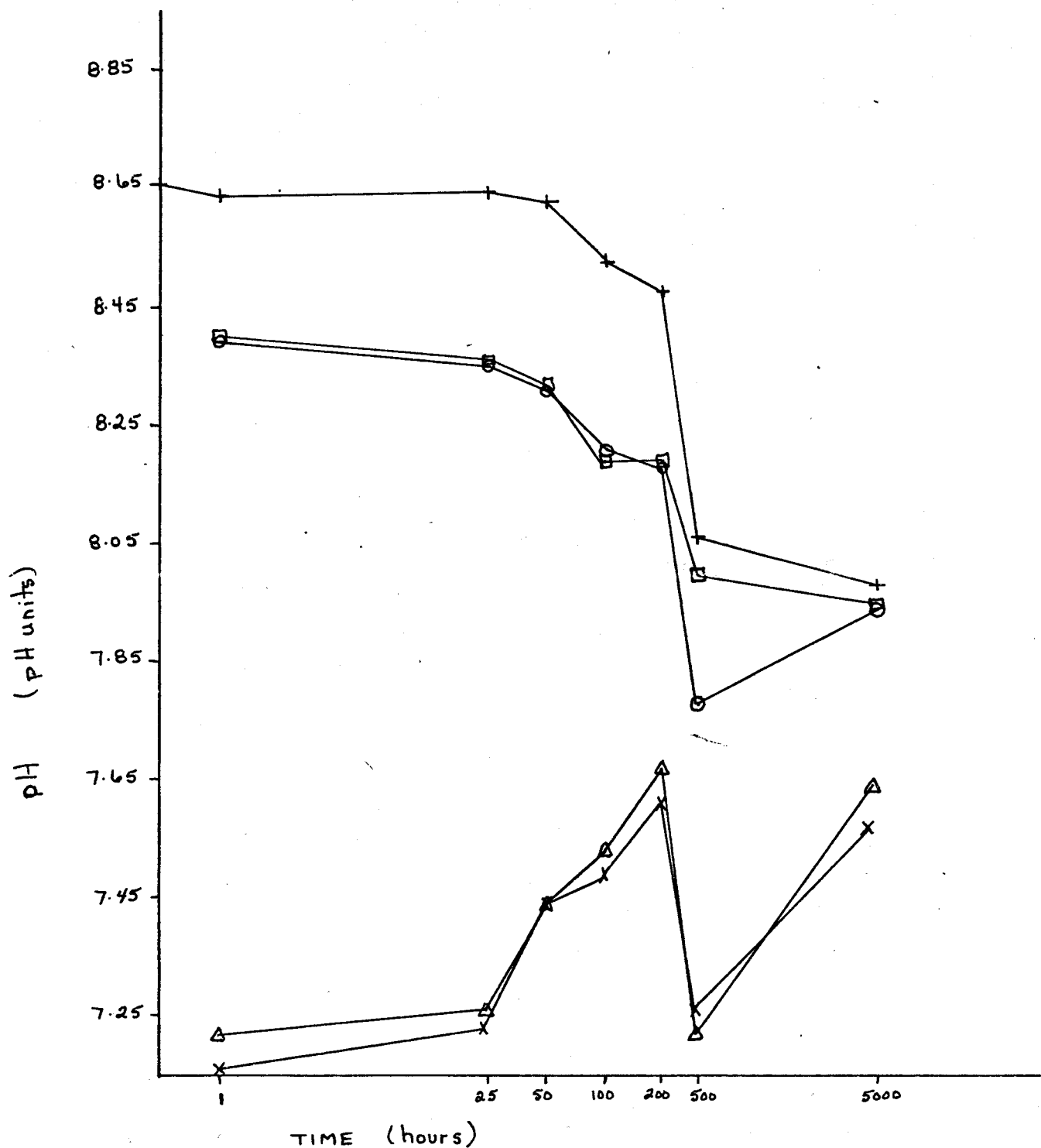


Figure II (d) + CONTROL

○ MONTMORILLONITE #13
◻ MONTMORILLONITE #14

Δ ILLITE #11 } DUPLICATE
X ILLITE #12 } SAMPLES

TABLE VI

Degree of calcite saturation for samples initially and after 5000 hours

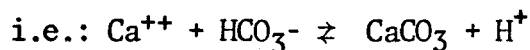
IAP / K_{Calcite}

	Initial	5000 Hours
Control	4.5	0.58
Illite	0.30	0.50
Montmorillonite	3.3	1.52

NOTES:

$\text{IAP}/K_{\text{Calcite}}$	> 1	Supersaturation
$\text{IAP}/K_{\text{Calcite}}$	= 1	Saturation
$\text{IAP}/K_{\text{Calcite}}$	< 1	Undersaturation

with respect to calcite was reached. The montmorillonite samples show the same trend. These data can be explained by the precipitation of CaCO_3 from solution.



This reaction also explains the trend in pH (see Figure II (d)). The degree of saturation of the illite samples show an initial undersaturation with respect to calcite. During the experiment the samples tended towards saturation. The pH trends (Figure II (d)) and the degree of saturation data (Table VI) both support the dissolution of calcite. The prime cause for the increase in Ca^{++} concentration in the illite samples is therefore the dissolution of calcite. The montmorillonite Ca^{++} increase is attributable to Ca^{++} release from the clay. (NOTE: for a more complete discussion of the Ca - calcite problem see Appendix I).

The pH data (Figure II (d)) can be explained by the attempt of the samples to reach equilibrium with respect to calcite. The Ca data (Figure II (b)) for the illites is also related to the equilibration of the system.

Cation Exchange Experiments:

The results of the cation exchange experiments are shown in Table VII.

The total cation exchange capacity of the illite shows a slight increase over 5000 hours. This is probably not significant. The important thing to notice is the trend of the elemental ratios. With the exception of K, all the elemental ratios i.e. $\frac{[\text{ELEMENT}]}{[\text{Na}]}$ have trended towards the elemental ratio for the artificial sea water.

The total cation exchange capacity for the montmorillonite decreases 17.9 meq/100 gms over 5000 hours. With the exception of Ca, there has been a trend towards equilibration of the exchangeable cations with the artificial sea water composition.

TABLE VII

CATION EXCHANGE CAPACITY AND EXCHANGEABLE CATIONS FOR MONTMORILLONITE
AND ILLITE AT ONE HOUR AND 5000 HOURS

(meq/ 100 gm.)					
SAMPLE	$\frac{K}{K/Na}$	$\frac{Na}{Na/Na}$	$\frac{Mg}{Mg/Na}$	$\frac{Ca}{Ca/Na}$	Total
ILLITE					
ONE HOUR	0.580	34.9	7.15	2.46	45.09
	0.017	1.0	0.205	0.070	-
ILLITE					
5000 HOURS	0.531	39.3	7.30	1.77	48.09
	0.135	1.0	0.186	0.045	-
MONTMORILLONITE					
ONE HOUR	5.31	51.6	39.1	8.35	104.36
	0.103	1.0	0.758	0.162	-
MONTMORILLONITE					
5000 HOURS	2.17	42.1	30.1	7.05	81.42
	0.052	1.0	0.715	0.167	-
ARTIFICIAL					
SEAWATER	-	-	-	-	-
	0.039	1.0	0.11	0.036	-

The decrease in cation exchange capacity of the clay with exposure to sea water has been found by other investigators (Carrol & Starkey (1958), Russell (1970)) and has been attributed to a strong bond between clay and K^+ which does not allow K to be exchanged using normal experimental procedures (Keller (1962), Sawhney (1971)).

X-Ray Diffraction

The X-ray diffraction data showed that there was no major mineralogical change for either mineral over the length of the experiment. This is consistent with the observations of Whitehouse and McCarter (1956) and MacKenzie et al (1965).

The illite diffraction patterns were monotonously similar under all conditions of the X-ray experiments, therefore their patterns are only presented for the illites X-rayed when moist (Figure III).

The montmorillonite X-ray diffraction patterns did show some interesting features which indicate minor alterations of the mineral.

The increased intensity and difuseness of the "5.0Å " peaks seen in the moist montmorillonite samples (see Figure IV (a)), suggest incipient illite formation. The montmorillonite also didn't expand fully to 17Å when glycolated (see Figure IV (c)).

This feature was noted by Biscaye (1965) of natural mixed layered montmorillonite/illites.

This infers however that the original montmorillonite is also a mixed layered montmorillonite/illite, as it expanded to only 16.27Å (see Figure IV (c)). The X-ray diffraction patterns of the montmorillonites at the end of this experiment bear little resemblance to those of the mixed layered montmorillonite/illites studied by Hower and Mowatt (1966) (see Figures IV (a) and (c)).

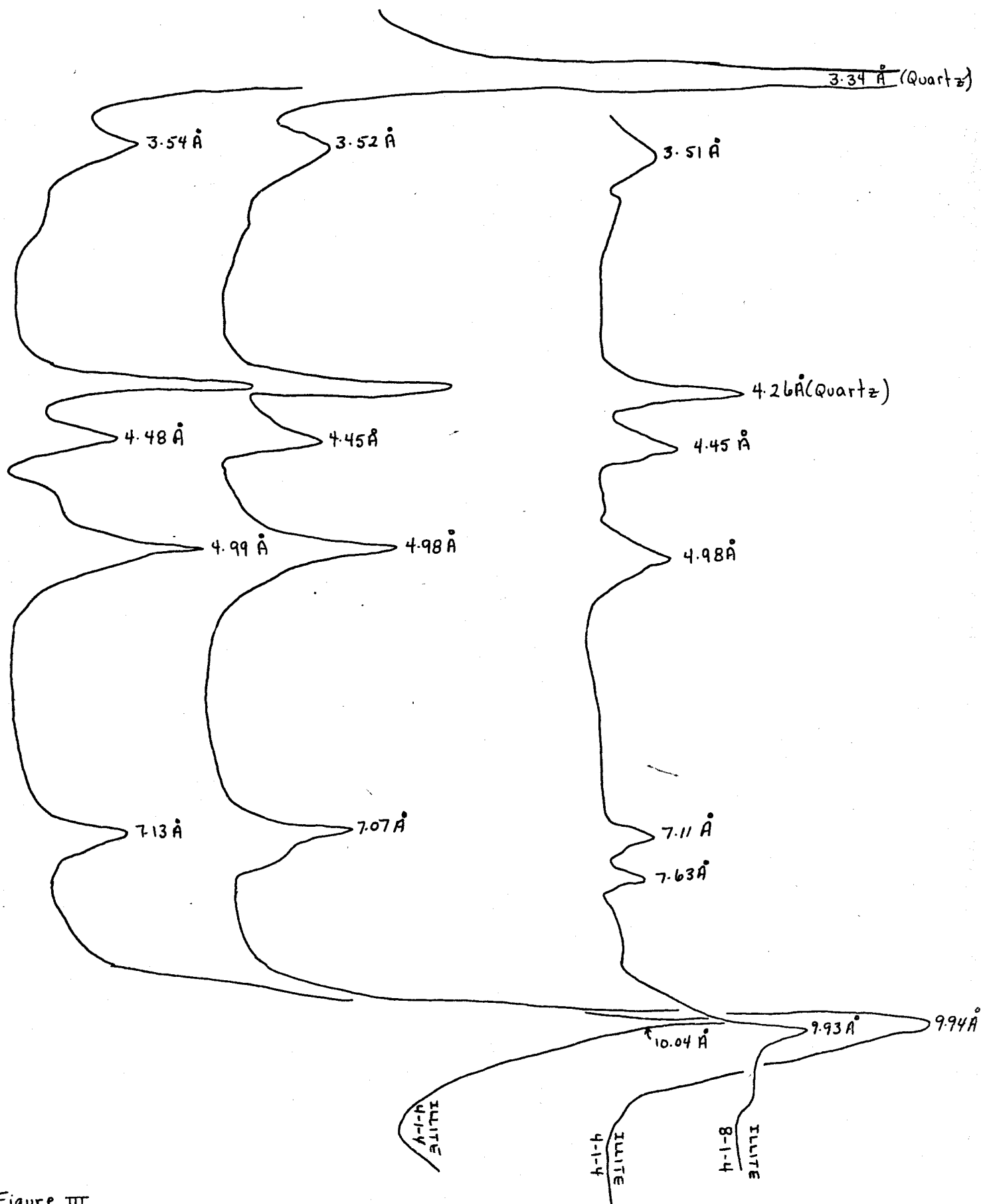


Figure III

Explanation of labels: Ex: ILLITE
8-1-4

8 = Multiplier ; 1 = TIME CONSTANT ; 4 = SCALE COUNTS/MIN

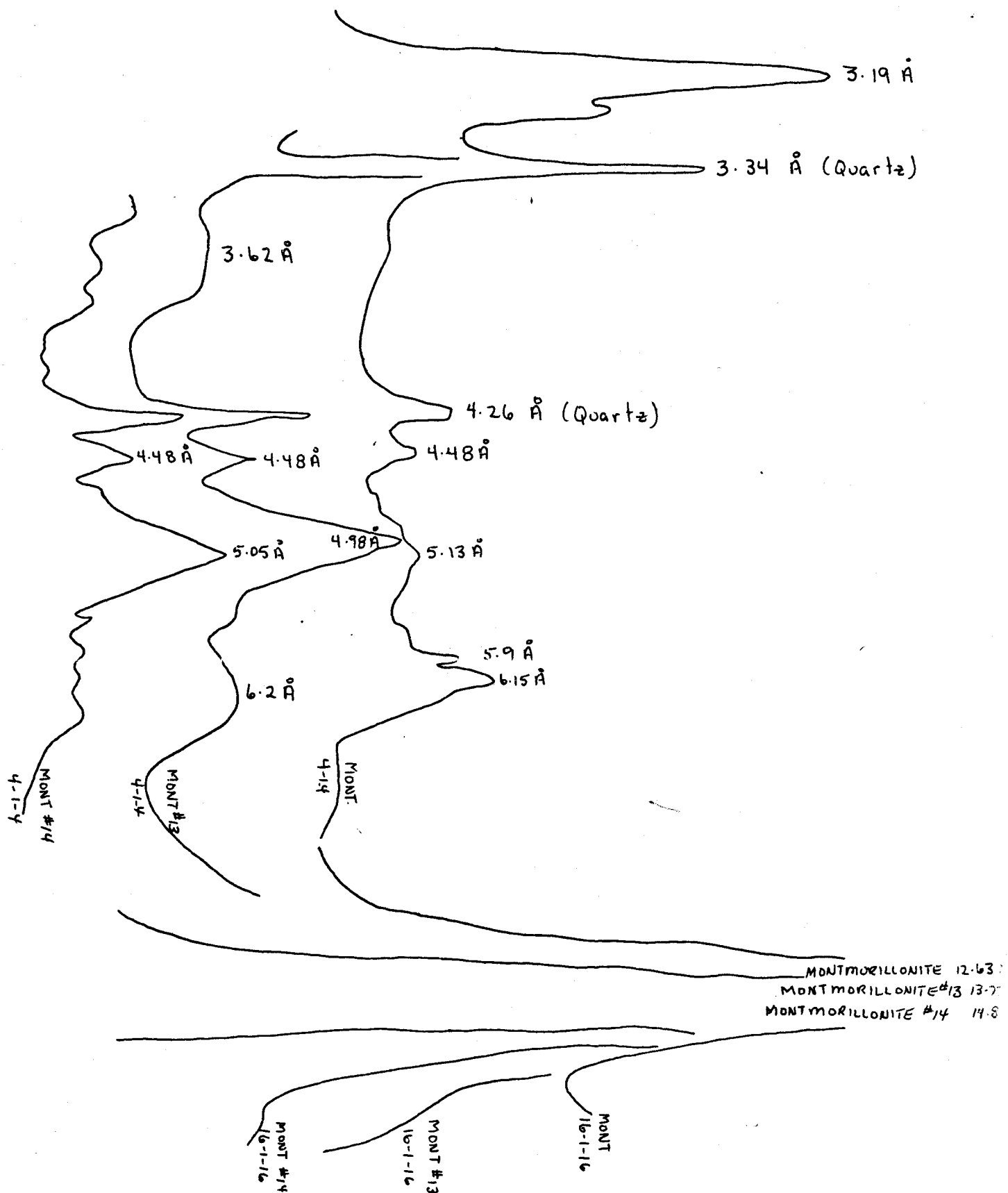


Figure IV (a) Explanation of labels: EX: MONT
16-1-16

16 ≡ Multiplier

1 ≡ TIME CONSTANT

16 ≡ SCALE COUNTS / MIN.

ORIENTED X-RAY DIFFRACTION PATTERNS FOR MONTMORILLONITE AFTER HEATING OVERNIGHT AT 150°C FIGURE IV (b)

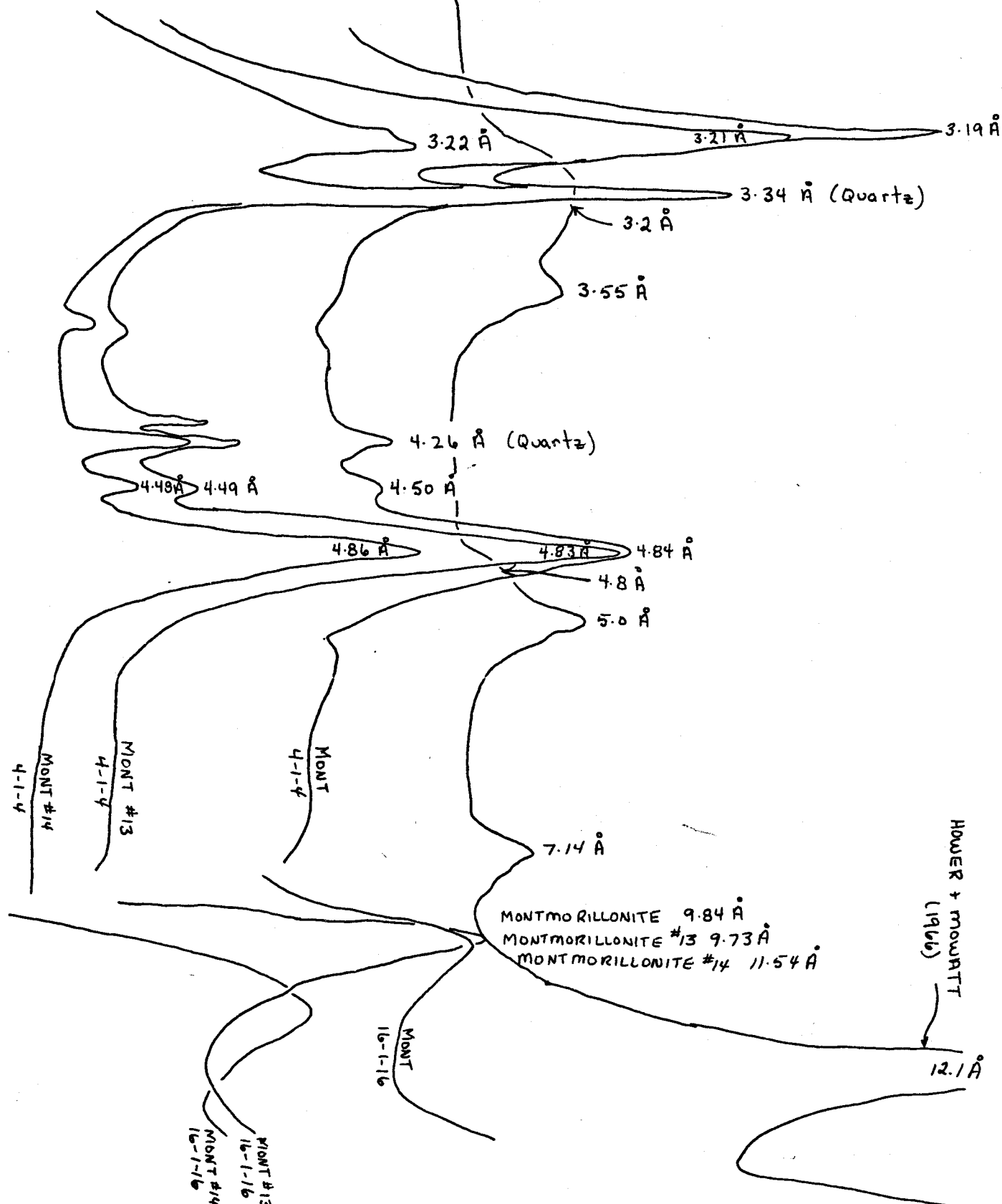


Figure IV (b) Explanation for labels; see Figure IV (d)

Howe + Mowatt (1966) = TWO MEDICINE (NO TREATMENT) = MIXED LAYERED
MONTMORILLONITE/ILLITE

ORIENTED X-RAY DIFFRACTION PATTERNS FOR MONTMORILLONITE (GLYCOLATED)

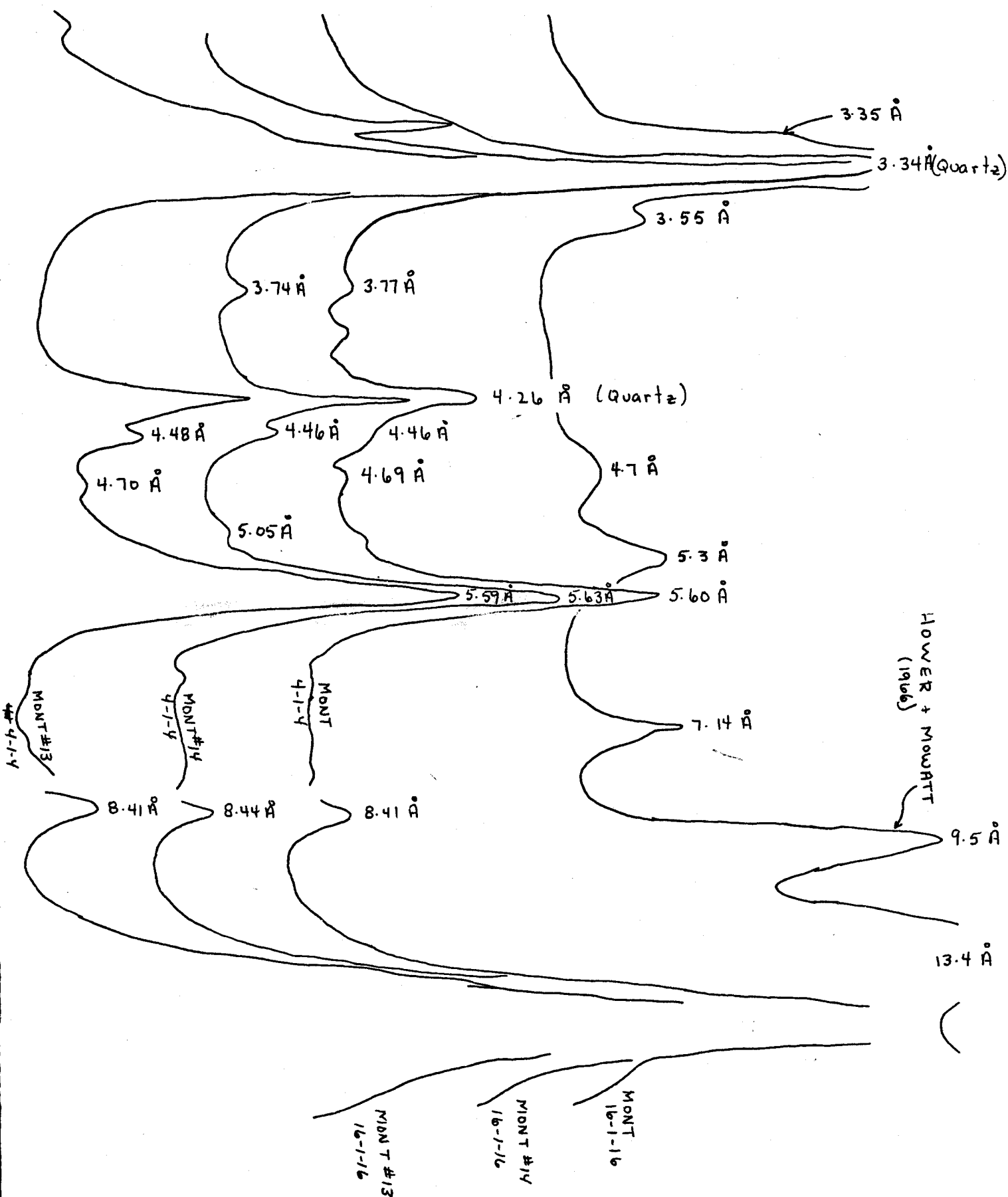


Figure IV (c) For explanation of labels see Figure IV (d)

HOWER + MOWATT (1966) = TWO MEDICINE (Glycolated) = MIXED LAYERED MONTMORILLONITE/ILLITE

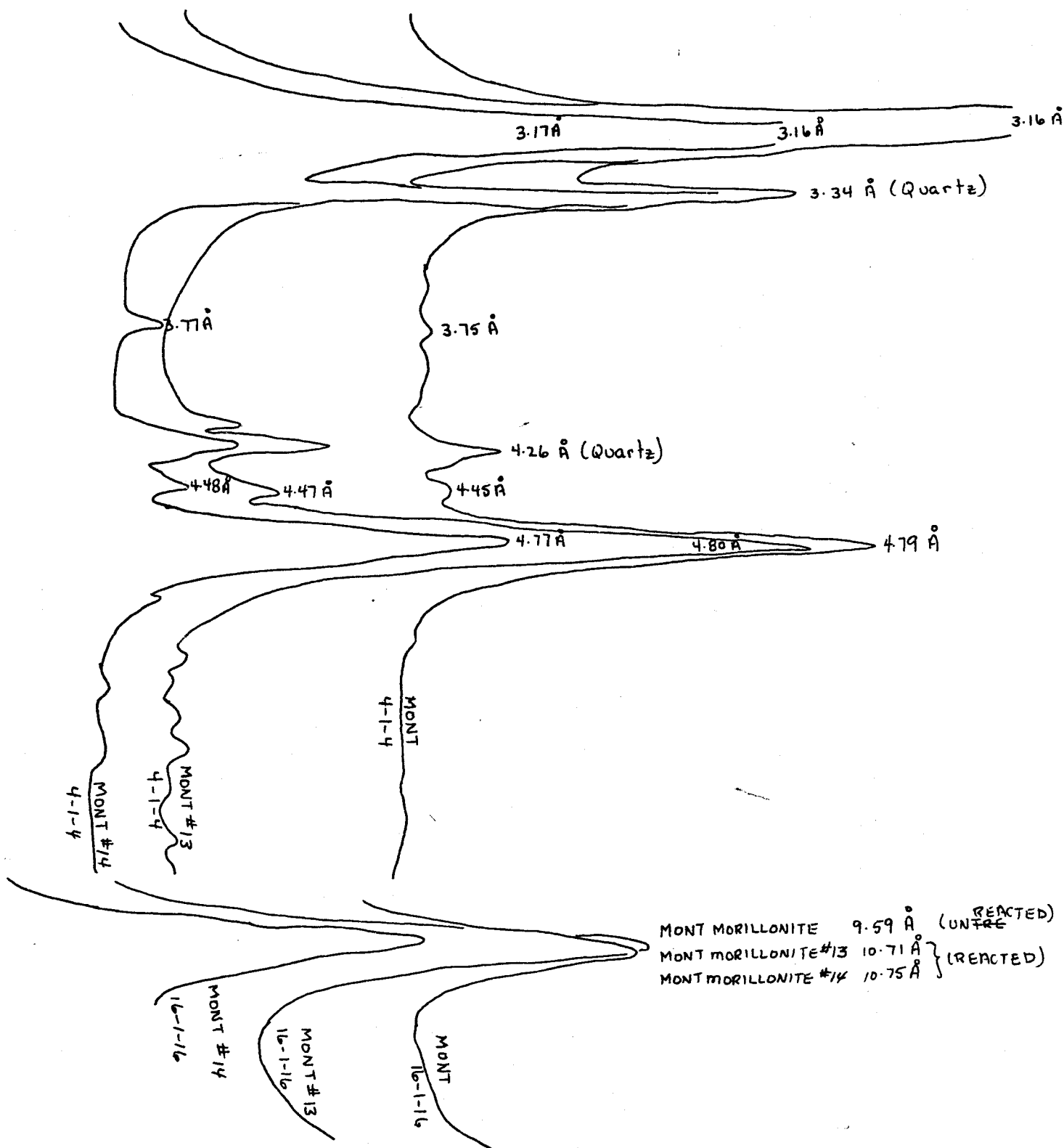


Figure IV (d)

Explanation of numbers under labels ex. MONT 16-1-16

16 = Multiplier

1 = Time Constant

16 = Scale of No. of Counts / min.

CONCLUSION

- (1) No major mineralogical change took place to either illite or montmorillonite during the 5000 hours of the experiment. The montmorillonite showed some evidence of incipient formation of illitic layers.
- (2) The composition of the clay sea water suspension is initially controlled by clay surface reactions, i.e.: surface hydration.
- (3) The exchangeable cations of the clays equilibrate with the composition of the artificial sea water.
- (4) The pH of the suspensions was controlled by the degree of saturation of the samples with respect to calcite.

DISCUSSION

The Ca and Si data for montmorillonite and the Si data for illite can best be explained in terms of a model discussed by Houston (1972) for the weathering of feldspars. The general form of the concentration vs. time curve for both Si and Ca is shown in Figure V (b) (Houston 1972). The initial hydration of the surface and the dissolution of the surface cations, causes a fast increase in the concentrations of all cations and is essentially complete within one hour. After one hour adsorption processes take over. Adsorption of cations continues until all sites are filled on the mineral surface. After this point the concentration of the solution depends upon the kinetics of dissolution.

Figure VI (a) and Figure VI (b) show the form of the curve for absorption and dissolution.

The Si data for illite shows no increase in concentration after the "peak". According to Houston's model, this indicates that the adsorption sites have not been saturated and that the adsorption is keeping pace with dissolution as shown in Figure V (a). If the samples had been washed before the experiment, the change of concentration with time would resemble Figure VI (b) because most of the cations absorbed on the surface would have been removed.

The dissolution of silica by clays in silica deficient sea water has been studied by MacKenzie and Garrels (1965). MacKenzie et al found that the silica concentration vs time curves were similar to Figure VI (b). They do not specify whether the clays were washed beforehand. Figure VII shows MacKenzie et al's data for illite and montmorillonite plotted alongside data from this study. The absolute values of silica concentrations at the end of 5000 hours are in good agreement. The silica data for illite indicates

FIGURE V

GENERAL FORM OF CONCENTRATION VS
TIME CURVES (HOUSTON (1972))

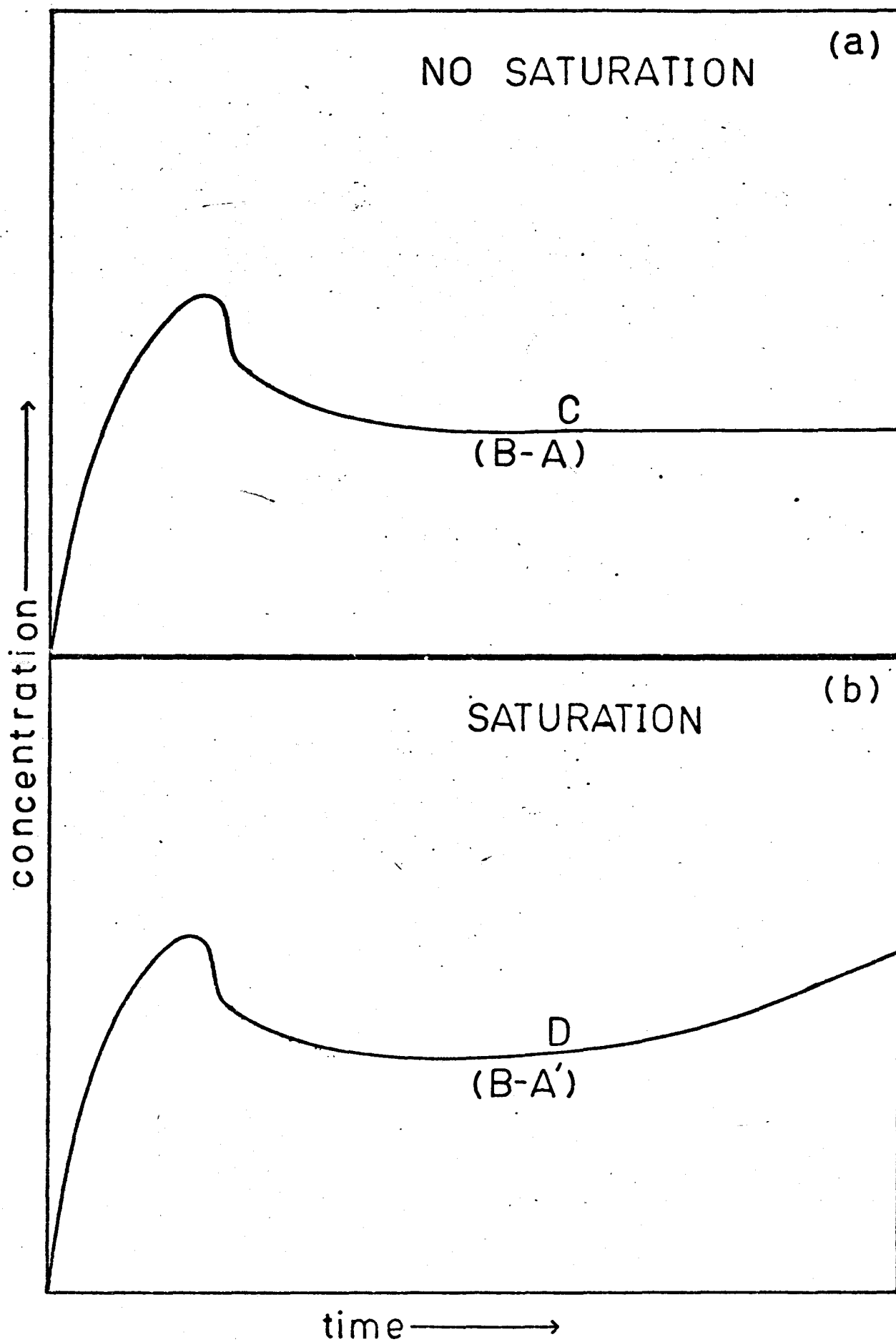


FIGURE VI FORM OF THE CURVES FOR
ADSORPTION AND DISSOLUTION (HOUSTON 1972)

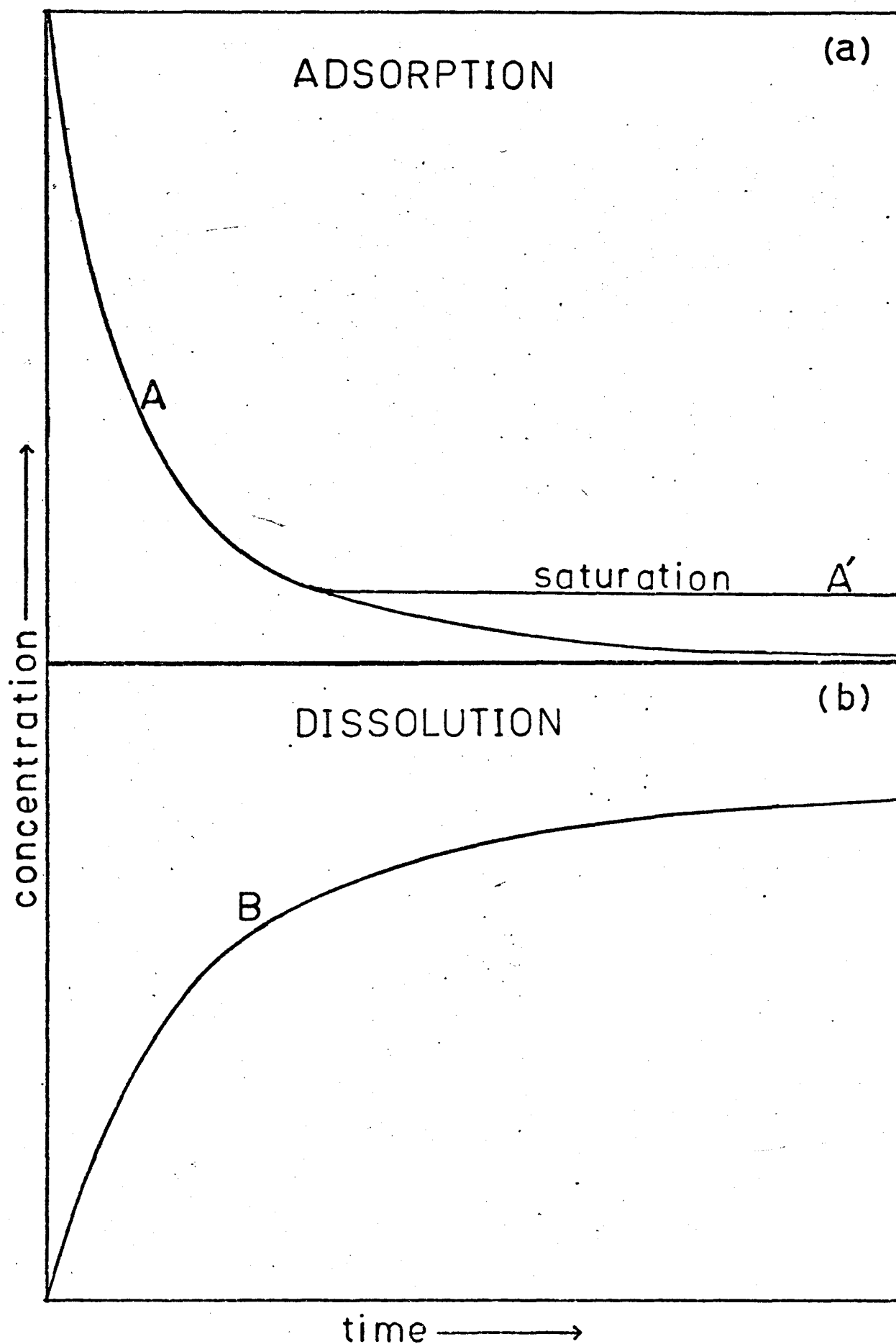
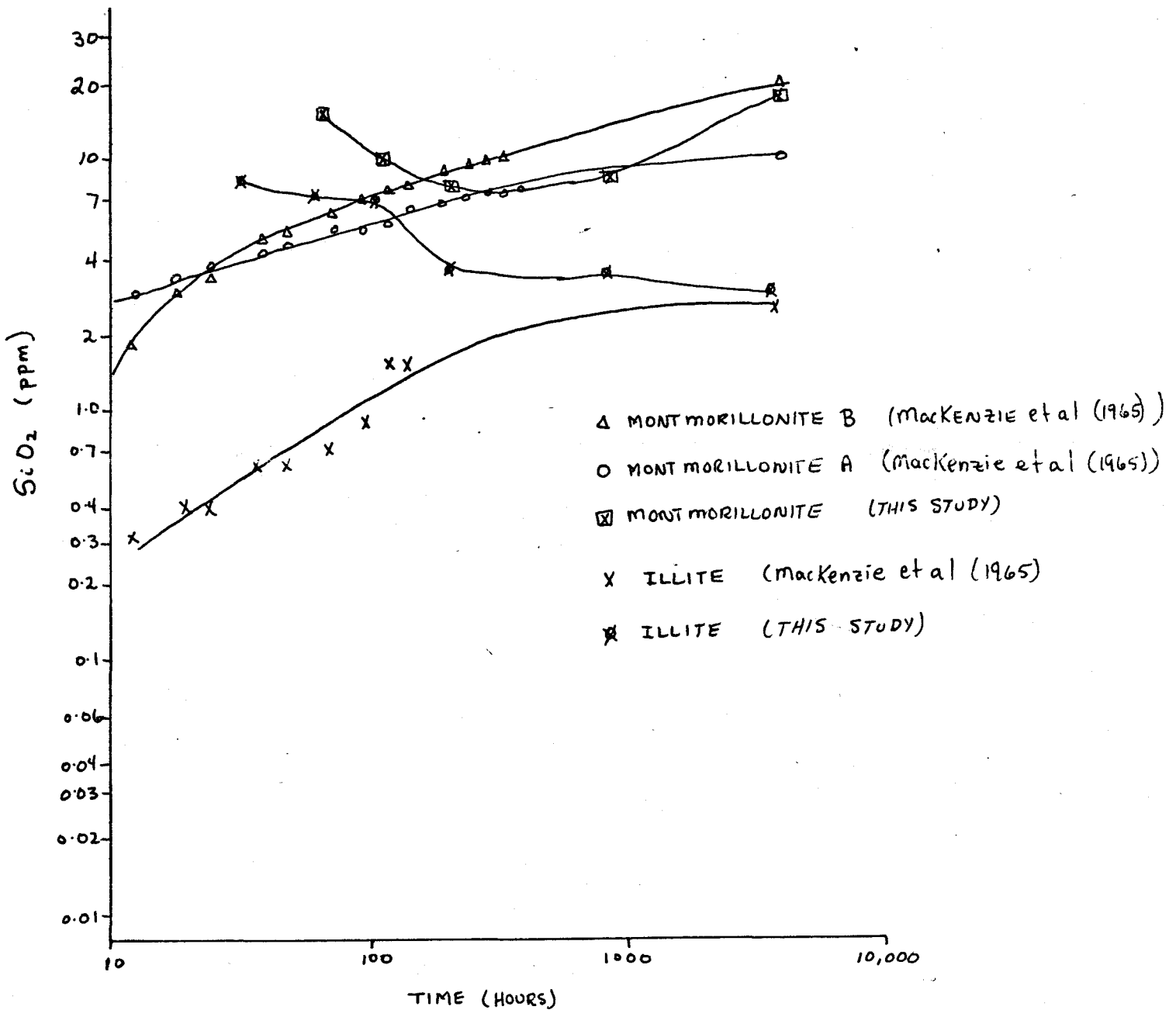


FIGURE VII

SILICA CONCENTRATION AS A FUNCTION OF TIME
FOR SILICATE SEA WATER SUSPENSIONS

MACKENZIE et al (1965) AND THIS STUDY



incongruent solution with the formation of an aluminous residue (MacKenzie & Garrels (1965)). Carrol & Starkey (1958) also showed preferential removal of silica from silicates.

MacKenzie and Garrels suggest that the higher silica values for montmorillonites indicates that their incongruent solution produces some substance other than an aluminous residue.

They speculate that their results represent the first stages of the transformation of the montmorillonite to an illitic or chloritic clay as described by Whitehouse and McCarter (1956). In a later paper, (MacKenzie et al (1967)) they describe the uptake of dissolved silica by clay minerals from sea water enriched in silica. From these observations it is apparent that clay minerals either release or take up silica depending upon its concentration in sea water. This could possibly be an indication that the concentration of dissolved silica in sea water is an important factor in the determination of the type of authigenic aluminosilicates formed.

The total cation exchange capacity for montmorillonite is in agreement with that determined by Lewis (1950) for the same A.P.I. clay. He found the montmorillonite exchange capacity to be 95.0 meq/100 gms. (total sample). He found the illite exchange capacity to be 25.0 meq/100 gms. (total sample). Whitehouse and McCarter (1956) found values of 148 to 151 meq/100 gms for the montmorillonite and 26 to 36 meq/100 gms. for the illite. The differences in the three values for montmorillonite can be explained by the different size fractions used. Lewis used the total sample. Whitehouse et al used the $<2\mu$ fraction and this study used the $<37\mu$ fraction. The decreasing particle size would effectively increase the cation exchange capacity by increasing the percentage clay in the sample. The discrepancy in the illite measurements cannot be explained in this manner. The absolute value of the CEC is much greater than observed by other authors.

The decrease in CEC for the montmorillonite can be explained by the fixation of K^+ (Keller (1962), Sawhney (1971)). This decrease in CEC for montmorillonite exposed to sea water has also been observed by Carrol and Starkey (1958) and Russell (1970). Sawhney (1971) noted that K^+ is not effectively replaced by NH_4^+ in vermiculites and degraded micas, because both ions have low hydration energies which cause interlayer dehydration and layer collapse. He also noted that montmorillonites with greater layer charge show a greater tendency to fix K^+ .

Mg, because it forms a relatively insoluble hydroxide, i.e. $Mg(OH)_2$ can be retained in the interlayer as a brucite sheet, (Keller (1962)) thusly forming a chloritic type clay from a montmorillonite. This reaction, although favoured by the alkaline environment of ocean water could be reversed in a low pH environment. Just such a process could explain the difference between alkalinity of the montmorillonites' supernatant water and the alkalinity of the control sample in the present study (see Table V).

A comparison of the elemental ratios of the exchangeable cations at one hour and 5000 hours for both illite and montmorillonite, show generally a trend towards equilibration with the composition of the artificial sea water. Table VIII compares the data from the present study with the elemental ratios found by other authors.

Agreement is good for the Mg/Ca ratio between this study and other authors. The K/Ca ratio is in the same order of magnitude as that for Russell's Rio Ameca River clay. The Na/Ca ratio for this study is unusually high.

Keller (1962) attributes the control of the composition of cations filling the exchangeable sites of a clay to two factors: (1) The concentration of the cation in the solution in which the clay is suspended and (2) The bonding characteristics and surface charge of the clay.

TABLE VIII

COMPARISON OF ELEMENTAL RATIOS OF EXCHANGEABLE CATIONS FROM THE
WORK OF VARIOUS AUTHORS.

Na	/	Mg	/	K	/	Ca	(mole ratios)
11.9	/	4.28	/	0.615	/	1.0	THIS STUDY (MONTMORILLONITE)
4.57	/	4.85	/	-	/	1.0	Carrol & Starkey (1958) (MONTMORILLONITE)
5.25	/	4.00	/	-	/	1.0	Carrol & Starkey (1958) (H-MONTMORILLONITE)
0.825	/	2.24	/	0.47	/	1.0	RUSSELL(1970) RIO AMECA RIVER CLAY (mostly montmorillonite)
2.0	/	5.17	/	2.0	/	1.0	RUSSELL(1970) Marine clay #211

On the basis of the difference of molal activities between river and ocean water, Keller calculated the free energy change accompanying the exchange of one equivalent of the four major ions.

	ΔF
Ca^{2+}	891 cal.
Mg^{2+}	-415 cal.
Na^{2+}	-4332 cal.
K^{2+}	-353 cal.

From these figures, it can be seen that Ca^{2+} should be released in preference for some other cation, which was observed in this study. The order of adsorption would be $\text{Na}^+ > \text{Mg}^{2+} > \text{K}^+$. This is the order seen in the exchangeable sites for the clays used in this study.

Montmorillonites, and degraded illites and micas, because of their high interlayer charge, can form a tight bond with the loosely hydrated K^+ ion and thereafter the K^+ ion becomes "permanently" fixed and incorporated in the clay crystal.

Keller (1962) regards ion exchange and the other processes described so far in this section, i.e. silica dissolution and K^+ and Mg^{++} fixation as the initial step in a two step mechanism in the diagenesis of montmorillonites.

The second step concerns changes in the clay crystal structure. The conversion of detrital to authigenic clay has not been documented in Recent sediments (Berner 1971). However the conversion of montmorillonite to a mixed layered montmorillonite/illite during later diagenesis has been found. (Perry & Hower 1970).

Hower and Mowatt (1966) first recognized that illite (i.e. with a distinct structure from dioctahedral micas) and montmorillonite were end members of a continuous mixed layered solid solution series. They speculated that mixed

layered clays may be stable rather than metastable structures.

The thermodynamics of montmorillonite/illite series has been studied by Helgeson and MacKenzie (1970) and Helgeson, Garrels and MacKenzie (1969). They devised a stability diagram shown in Figure VIII. This diagram has been criticized by Perry(1971) as not being consistent with observations of Recent sediments.

The stability field for the montmorillonite/illite field is probably close to where it should be and the diagram does illustrate the continuous series and the dependence of authigenic formation of minerals on the silica concentration.

The stability of montmorillonite and illite over the short term (6 months) has been ascertained by this study and supported by the investigations of others in the laboratory (Whitehouse & McCarter (1956), Carrol & Starkey (1958), MacKenzie et al (1965) (1967) and Russell (1970)) and in the field. (Weaver (1958), Griffin (1962), Biscaye (1965) and Russell (1970)) and is supported by Sr and O isotope data (Dasch (1969) and Savin & Epstein (1970)).

The thermodynamic data of Helgeson et al (1969) & (1970) suggest that a mixed layered montmorillonite/illite is a stable mineralogical phase in sea water. If this is the case, then we must look for reasons why authigenic formation from detrital minerals is not seen. Kinetics, is the first factor which should be considered. Whitehouse and McCarter (1956) found that the absorption of carbohydrates by montmorillonite inhibited the formation of authigenic clays. Perry & Hower (1970) found the gradual formation of mixed layered montmorillonites/illites during burial diagenesis of Tertiary sediments.

Whitehouse and McCarter (1956) also noted that the rate of formation of authigenic clays from montmorillonite was fastest for samples kept in continual

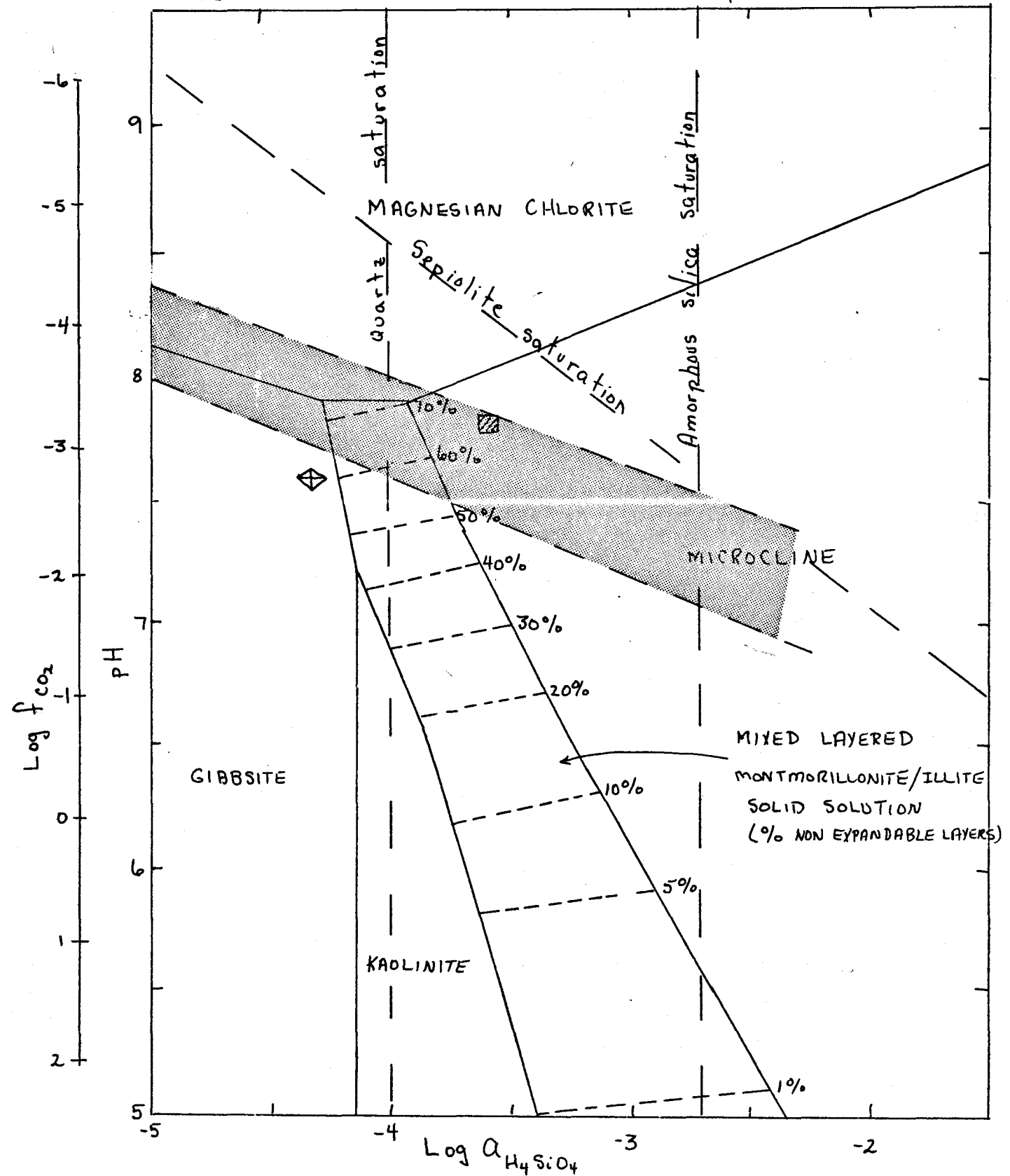
FIGURE VIII
STABILITY DIAGRAM FOR MONTMORILLONITE / ILLITE SOLID SOLUTION SERIES

From (Helgesen et al (1970)) AT 25°C

stippled area represents range of sea water composition

◈ final composition illite samples

▨ final composition montmorillonite samples



suspension, and that the rate decreased for samples suspended only part of the time and was slowest for samples allowed to sediment.

The studies by Whitehouse & McCarter (1956) and Perry & Hower (1970) suggests several paths for future research: the effects of the oceans' dissolved organic components, the effects of temperature and pressure, and the effects of continuous or intermittent suspension of clays on the rate of authigenesis.

Biscaye (1965) notes the importance of resuspension and transport of deep ocean sediments for the distribution of clay minerals in the ocean basins. He was writing in context of distribution of detrital minerals but this process could also be equally important in the formation authigenic clays from detrital clays. The resuspension and transportation process results in the extension of the suspended life time of a clay particle from that calculated from settling velocities. This much extended period of suspension may be all that is needed to form authigenic clays from detrital clays. The formation of authigenic clays could be directly related to the presence of nepheloid layers in ocean basins and is probably one of the fields of study which could lead to the resolution of when and where authigenesis of detrital mineral takes place.

APPENDIX I

Discussion of the Alkalinity decrease in illite samples:

The pH vs time curve for the illite samples shows that the pH of the sample was lowered from 8.64 to 7.22 in the first hour. There is also the possibility that the pH could have been much lower. This lowering of the pH can be caused by one of two things.

- (1) Contamination of the sea water by strong acid like that used to clean the bottles, or
- (2) Release of H^+ by the illite when placed in sea water.

The supernatant sea water is noticeably undersaturated with respect to calcite at one hour. This caused the dissolution of calcite from the sample i.e. $CaCO_3(s) + H^+ \rightleftharpoons HCO_3^- + Ca^{++}$

A one to one correspondence exists between the alkalinity at 5000 hours and the change in Ca^{++} concentration.

In the bottle there is 0.57 meg HCO_3^- ; the change in Ca^{++} is 1.22 meg Ca^{2+} or 0.61 mmoles.

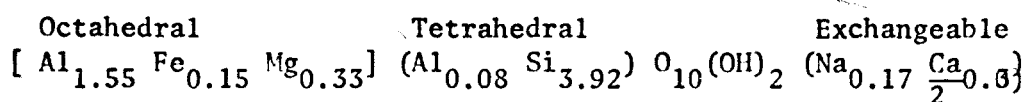
From this stoichiometry, it can be concluded that the present alkalinity in the sample is a direct result of the dissolution of $CaCO_3$. Therefore it is proposed that any initial alkalinity in the sample was lost by degassing in the first hour of the experiment caused by the lowering of the pH.

APPENDIX II

CHEMICAL ANALYSES OF CLAY MINERALS USED

MONTMORILLONITE #25b

	I	II	III
SiO ₂	57.49	58.56	59.34
Al ₂ O ₃	20.27	18.25	18.52
Fe ₂ O ₃	2.92	2.82	2.86
FeO	0.19	0.0	0.0
MgO	3.18	2.30	3.21
CaO	0.23	0.41	0.22
Na ₂ O	1.32	2.60	1.34
K ₂ O	0.28	0.55	0.77
H ₂ O ⁺	6.85	7.53	7.35
H ₂ O ⁻	7.63	14.45	13.60
TiO ₂	0.12	0.08	0.08



I Kerr et al (1950)

II Whitehouse & McCarter (1956) less than 2 microns

III Whitehouse & McCarter (1956) less than 2 microns after exposure to seawater for 6 months

APPENDIX II (continued)

ILLITE # 35

	I	II	III
SiO_2	56.91	52.75	52.54
Al_2O_3	18.50	24.83	24.73
Fe_2O_3	4.99	4.12	4.11
FeO	0.26	0.26	0.25
MgO	2.07	2.29	3.14
CaO	1.59	0.32	0.12
Na_2O	0.43	0.35	0.24
K_2O	5.10	5.71	6.42
H_2O^+	5.98	7.94	7.81
H_2O^-	2.86	8.79	7.96
TiO_2	0.81	0.62	0.60

I Kerr et al (1950)

II Whitehouse & McCarter (1956) less than 2 microns

III Whitehouse & McCarter (1956) less than 2 microns after exposure
to seawater for 6 months

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