

EQUILIBRATION OF CLAYS IN NATURAL AND SIMULATED BOTTOM-SEDIMENT ENVIRONMENTS

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Abstract—To identify mineral alterations which might occur in stream environments, predominantly illitic soil clays were equilibrated in bottom sediment environments under natural and laboratory conditions for 217 and 98 days, respectively. Changes occurring after 217 days on the bottom of the Auglaize River, Ohio, consisted of a reduction in carbonate content, a decrease in particle size, and a slight loss of Al and Si; however, no significant changes in basal spacings were observed.

Clays equilibrated in river water under laboratory conditions at 4° and 25°C in CO₂, N₂, or air atmospheres showed only an increase in oxalate-extractable iron. The concentrations of Al, Si, Fe, Mn, K, and Ca in solution above the clays varied with the atmosphere and temperature. The concentrations of Fe, Al, and Si in solution may have been influenced by the dissolution of amorphous Al-Fe-Si compounds. Therefore, the mineralogical differences between soils in the watershed and sediments in the drainage system can not be attributed to mineralogical transformations during residence in the drainage system.

Key Words—Alteration, Bottom sediments, Dissolution, Illite, Vermiculite.

INTRODUCTION

The clay mineralogy of stream and estuary sediments has been employed as an indicator of provenance; however, either clay mineral alteration within the fluvial environment or differential transport of clay minerals can lead to erroneous interpretations. Frink (1969) and Lietzke and Mortland (1973) indicated that dechloritization of chloritized vermiculite can occur when clay minerals eroded from acid soils are deposited in alkaline environments. Frink (1969) further suggested that dechloritized vermiculite was subsequently converted to illite in a eutrophic lake as indicated by higher illite content and correspondingly lower vermiculite content in the lake sediment relative to surrounding soils. Murad and Fischer (1978) suggested that in the Schwarzsach Valley of Germany, soil chlorites convert to illite by removal of interlayer Al and subsequent uptake of K in the river environment. Although these studies support mineral alterations in fluvial environments, they are not conclusive due to possible confounding by differential transport of clay minerals. Rhoton *et al.* (1979) showed that illite and expandable clays are selectively transported from soil surfaces, a phenomenon that can explain mineralogical differences between sediment and soil clay.

Wall *et al.* (1974) equilibrated a soil clay fraction with sewage effluent in a static laboratory system and found that clay mineral alteration was closely related to microbiological activity. The alterations resulted in a decrease in the relative percentage of mica, expandable clays, and vermiculite and an increase in the percentage of quartz and chlorite.

Because the Maumee River drainage system of

northwestern Ohio is characterized by a low gradient, a high concentration of flocculating ions, and numerous impoundments which increase the residence time of sediments, clay mineral alteration should be favored. The objective of this study was to evaluate the type and magnitude of clay mineral alterations occurring under natural bottom-sediment conditions within the Maumee River drainage system and to compare these alterations with those found in the laboratory under different aqueous environments.

METHODS AND MATERIALS

Stream bottom equilibration

Twenty-gram samples of Mg-saturated clay (<2 μm) from the calcareous C-horizon of a Hoytville pedon (Mollic Ochraqulf) (the most extensive soil in the Maumee River basin) were placed in Plexiglas cylinders (5 cm × 20 cm). Nucleopore membranes attached to each end of the cylinders by rubber O-rings confined the samples and permitted free ionic exchange between the clay and the fluvial environment without gain or loss of solids. The cylinders were attached by spring-type clips to a Plexiglas plate which was surrounded by a fiberglass screen. Scuba divers staked the plate at the sediment-water interface upstream from the Edison Power Dam on the Auglaize River, a tributary of the Maumee River. Individual cylinders were retrieved by divers at intervals of 38, 148, 217, and 281 days. The equilibrated clay samples were compared to the original samples using: clay mineralogy; broadening of the 001 illite peak; cation-exchange capacity (CEC); calcite and dolomite content; amorphous alumina and silica content, oxalate-extractable iron (Fe_o) and free iron oxide (Fe_f) content; external surface area; and total Fe, Al, Si, and K content.

Laboratory equilibration

Approximately 3300 g of untreated Auglaize River bottom sediment and 13 liters of river water were placed in each of 10 aquaria (18.9-liter capacity) and equilibrated for one week at 4°C in either air, N₂ (99.9%), or CO₂ (20%) atmospheres. The gases, bubbled through tygon tubing at the sediment-water

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interface, induced environments which may exist under natural bottom-sediment conditions. The CO₂-rich atmosphere simulated the environment in the vicinity of organic-rich sediments which release CO₂ as a result of microbial decomposition. The N₂ and compressed air atmospheres created environments at opposite ends of the redox potential scale.

After allowing the sediment and water to equilibrate for one week, 3 Plexiglas cells containing 15 g of either Hoytville A or C horizon clay were partially submerged in the sediment of each aquarium. Only calcareous C-horizon clays were equilibrated in the CO₂ aquaria. Once the cells were in place, the aquaria were sealed with Plexiglas lids. N₂ was bubbled through 4 aquaria daily for 12 hr, whereas CO₂ was bubbled through 2 aquaria for 6 hr daily and then shut off for 18 consecutive hours. Air was bubbled continuously through the other 4 aquaria. All aquaria were equilibrated for 45 days at 4°C at which time 5 (2 air, 2 N₂, 1 CO₂) were discontinued because all clay cells had been retrieved. The remaining 5 aquaria were equilibrated for an additional 53 days at 25°C. Temperature changes were induced to simulate seasonal effects.

Water samples and clay cells were removed periodically at each temperature. Water samples were withdrawn in 200-ml aliquots at a constant distance above the sediment-water interface. Aliquots from 5 aquaria were collected frequently (at days 1, 3, 5, 7, 14, 21, 28, 45), whereas aliquots from the other aquaria were collected only occasionally at 4°C (at days 1, 21, 45), but more frequently at 25°C (at days 49, 54, 69, 85, 98). Reference water samples were collected from each aquarium immediately prior to adding the clay cells. Individual cells were removed for analysis at approximately two-week intervals at 4° and 25°C. All water and clay samples were stored at 4°C until analyses were completed.

Water samples were analyzed for: dissolved Si, Fe, Al, Mn, Ca, and K. Clay samples were analyzed for: Fe_o, Fe_a, total Si, Al, Fe, K, Ca, and calcite and dolomite contents. Redox potential and pH measurements were made on the sediment and solution before the cells were added to the aquaria; thereafter, these parameters were determined only for the solution phase at the time of sampling.

Analytical techniques

Clay samples equilibrated in the river were saturated with Mg and washed with methanol prior to and after equilibration. X-ray powder diffraction (XRD) analyses were made with Ni-filtered CuK α radiation using a Norelco diffractometer equipped with a 0.0006 inch receiving slit, a 1° divergence slit, and a proportional counter and using a chart speed of 1°2 θ /min. Sample preparation consisted of vacuum plating 0.15 g of clay on ceramic plates (Kinter and Diamond, 1956). Sample treatments included saturation with ethylene glycol, air drying at 25°C, heating to 400°C, and heating to 550°C. Relative percentages of illite, vermiculite/chloritized vermiculite, kaolinite, and quartz were determined by the method of Johns *et al.* (1954) as modified by estimating quartz by the 3.3-Å peak after third order mica contributions had been subtracted. The vermiculite/chloritized vermiculite phase is characterized by a 14.0–14.7-Å peak with ethylene glycol treated clay. This phase consists of vermiculite and a poorly crystallized component that does not fully collapse to 10 Å when heated to 400°C. Peak areas were measured according to symmetry and average baseline heights. Photocopies of the peaks were weighed and clay mineral percentages reported as a mean of ten subsamples extracted from each cell and analyzed separately. Measurements of peak broadening were made by the procedure of Jackson (1977).

CECs were determined by the sodium saturation method of Chapman (1965) after dialyzing the clays against a 10% solution of acetic acid to remove carbonates. Calcite and dolomite contents were obtained with the Chittick apparatus (Dreiman-

is, 1962). Oxalate-extractable iron (Fe_o) and free iron oxides (Fe_f) were extracted with 0.2 M ammonium oxalate (McKeague and Day, 1966) and citrate-bicarbonate-dithionite (Mehra and Jackson, 1960), respectively, and quantified by atomic absorption spectrophotometry (AA). Amorphous alumina and silica were determined by treating clays with 0.5 N NaOH (Hashimoto and Jackson, 1960). Total elemental analyses were determined by decomposing samples with HF and aqua regia in a Teflon bomb (Bernas, 1968) and analyzing the solution by AA. External surface area (BET) was measured by Micromeritics Instrument Corporation, Norcross, Georgia.

Dissolved Si, Al, Fe, and Mn were determined by the colorimetric method of Rainwater and Thatcher (1960). Dissolved K and Ca were determined by emission spectroscopy and AA, respectively. Redox potential and pH were measured by inserting platinum wire or glass electrodes with calomel cells through holes (otherwise stoppered) in the aquarium lids into the water. Redox potentials were read from the millivolt scale of the pH meter after insuring that the platinum electrode had equilibrated.

RESULTS AND DISCUSSION

Stream bottom reactions

The equilibration of clays at the sediment-water interface was intended to last for two years, but nearly all of the cells were lost due to flooding between 217 and 281 days; only 1 cell survived. Therefore, only 4 cells were collected at intervals of 38, 148, 217, and 281 days. The cell collected at 281 days was contaminated; therefore, these data are not included in the present discussion.

The clay mineralogy of these samples (Table 1) reveals only slight variations with time which are well within the margin of error for such semi-quantitative analyses. The lack of significant mineralogical changes may be due to the relatively short equilibration period; however, sediment residence time in the Maumee River system is believed to be of a similar magnitude. Correlation coefficients (*r*) calculated for the change in elemental composition with equilibration time indicate some statistically significant trends (Table 2). Significant changes occurred in total Al (5% confidence level) and Si (1% confidence level) as both decreased through 217 days. Total Fe and K changed little with time. The lack of a decrease in K may indicate that Al and Si are lost as a result of surface reactions that do not influence interlayer K. Small increases occurred in Fe_o and Fe_a; however, they were not significant at the 5% confidence level. Amorphous alumina showed little change with time, whereas, amorphous silica appeared to increase; however, the values were erratic and nonsignificant (5% confidence level).

External surface area and carbonate content as a function of equilibration time are listed in Table 2. Although the increase in surface area, which is nonsignificant at the 5% level, suggests a decrease in particle size, the decrease may be influenced more by the progressive dissolution of carbonates than by clay mineral decomposition. Carbonate analyses indicate that the

Table 1. Mineralogical composition of clays equilibrated in the Auglaize River.¹

Length of equilibration (days)	Vermiculite-chloritized vermiculite (%)	Illite (%)	Kaolinite (%)	Quartz (%)
0	17	76	2	5
38	15	75	2	8
148	16	76	2	6
217	17	73	4	6

¹ Mean of ten subsamples from each cell which were analyzed individually.

calcite content decreased at a slightly greater rate than dolomite. Wall *et al.* (1978) believed that carbonate dissolution in bottom sediments in the Maumee River drainage system was the result of relatively high CO₂ concentrations due to the decomposition of organic matter. However, the precipitation of secondary calcite was reported in the suspended sediments of the Maumee River drainage system by Wall and Wilding (1976) and Green and Smeck (1979) and attributed by the latter to a lowering of the CO₂ concentration near the stream surface by aquatic biomass production. Thus, calcite that precipitates near the stream surface is apparently dissolved before or after reaching the stream bottom. The CEC fluctuated considerably, indicating no trends as a function of time or correlation with surface area.

Broadening of the 001 peak of illite from the air dry treatments (Table 3) suggests a decrease in particle size. Thus, the increase in external surface area and the decrease in total Al and Si may be related to clay mineral degradation which would presumably occur as a surface hydrolysis reaction disrupting the 001 reflection plane. However, because peaks of other clay minerals also decreased in intensity, the peak broadening may be the result of an increase in the content of amorphous materials. Iron oxides were not removed prior to XRD analysis; therefore, these materials could contribute to the observed peak broadening by decreasing basal diffraction intensity (Jackson, 1975). The latter hypothesis is supported by the lack of a decrease in K content which would be expected to accompany disruption of the 001 reflective plane; however, no significant change in iron oxide content was found through 217 days.

Table 2. Total elemental Fe, Al, Si, and K, external surface area, and carbonate content of clays equilibrated in the Auglaize River.

Length of equilibration (days)	Total (mg/g clay)				Surface area (m ² /g)	Carbonates	
	Fe	Al	Si	K		Calcite (%)	Dolomite (%)
0	49.0	112	198	29.0	46.1	7.0	4.0
38	49.0	110	197	29.0	¹	8.2	2.3
148	48.5	105	183	29.8	48.2	6.6	3.0
217	49.8	99	173	30.4	51.9	4.9	2.8

¹ Surface area measurements were not obtained for the sample equilibrated 38 days.

Table 3. Measurement of 001 illite peak broadening for clays equilibrated in the Auglaize River for 217 days.

Replication	Peak height (mm)		Width at ½ peak height (mm)	
	Reference	217	Reference	217
1	186	149	5.5	5.0
2	186	132	4.8	4.5
3	190	142	5.3	4.8
4	181	128	5.0	5.5
5	191	139	4.8	5.0
6	197	141	4.5	5.0
7	176	147	4.8	5.0
8	190	141	5.0	5.3
9	178	158	5.5	5.0
10	184	138	4.8	5.5
Mean	185.9	141.5	5.0	5.1
Width/height ¹	0.026	0.036		

¹ Calculated from mean values.

Laboratory equilibration

The Fe_o contents of laboratory equilibrated A- and C-horizon clays differ substantially (Table 4). Fe_o of the C-horizon clays remained unchanged except under the CO₂ atmosphere where a slight, but statistically significant (1% level) increase was noted. This increase corresponds to a slight but nonsignificant increase in Fe_o in the clays equilibrated in the river. The Fe_o content of A-horizon clays increased substantially, especially in the N₂ atmosphere. Correlation coefficients indicated significance at the 1% and 5% level for the N₂ and air atmospheres, respectively. In all experiments, most of the increase occurred after the temperature was increased to 25°C.

The initial redox potential of the aquarium sediments was less than -300 mV. The redox potential of the overlying water in the N₂ atmosphere eventually decreased to less than -400 mV compared with +300 mV for other atmospheres. Because the aquarium systems met the criteria for FeS formation (Connell and Patrick, 1968; Doner and Lynn, 1977), the increase in Fe_o content of A-horizon clays in the N₂ atmosphere is believed to be due to development of low redox potentials in the overlying water which permitted sulfide and ferrous iron to diffuse across the sediment-water interface

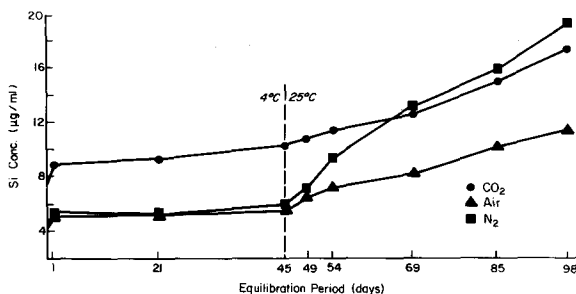


Figure 1. Concentration of Si in river water placed in aquaria containing clays as a function of time, temperature, and atmosphere.

where FeS precipitated in the cells. Numerous black aggregates, presumed to be FeS, were dispersed throughout some samples; however, the susceptibility of FeS to acid ammonium oxalate is unknown. The lack of substantial increases in Fe₀ in C-horizon clay cells equilibrated in the N₂ atmosphere may be related to free carbonates maintaining the pH near the upper limit of the FeS precipitation range. Conversely, the increase in Fe₀ noted in C-horizon clays in the CO₂-rich atmosphere may be attributed to a lowering of the pH by the relatively high CO₂ content.

No trends were observed in the Fe_d content of either the A- or C-horizon clays regardless of temperature or equilibrating atmosphere. The calcite and dolomite content of C-horizon clays equilibrated in the laboratory did not appear to be affected by treatment. Total elemental analysis of A- and C-horizon clays revealed no trends, other than a decrease in the total Al content of C-horizon clays which was statistically significant (1% level) in the N₂ and air atmospheres.

Water-soluble Si, Al, Fe, Mn, Ca, and K was monitored in all aquaria at 4° and 25°C. Redox potentials and pH were recorded immediately before extracting water samples for elemental analysis. Si concentrations in solution at 4°C were substantially higher in the CO₂ atmosphere than in the N₂ or air atmospheres (Figure 1), which contained similar concentrations. The Si concentration for all treatments increased considerably after the temperature was increased to 25°C. However, at 25°C, the solution in the N₂ atmosphere contained considerably more soluble Si than the solution in the air

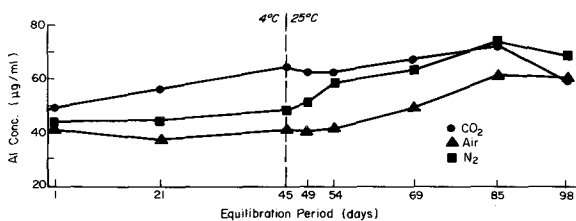


Figure 2. Concentration of Al in river water placed in aquaria containing clays as a function of time, temperature, and atmosphere.

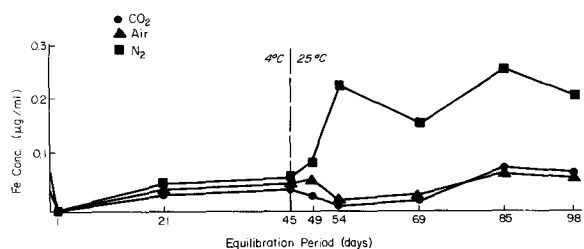


Figure 3. Concentration of Fe in river water placed in aquaria containing clays as a function of time, temperature, and atmosphere.

atmosphere and slightly more than the solution in the CO₂ atmosphere after 98 days. Trends for Al concentrations in the solutions in the various atmospheres as a function of time and temperature were essentially the same as those for Si; however, the differences were not as great (Figure 2).

Solution pH over the sediments varied from 6.1 to 6.5 for the CO₂ system, 8.0 to 8.4 for the air system, and 8.4 to 9.3 for the N₂ system. Sediment pH readings for these systems were 6.6, 7.6, and 7.9, respectively, after equilibrating for one week. Because the solubility of amorphous SiO₂ is essentially constant below pH 9.0, the relatively high concentrations of Si and Al in the CO₂ system may be due to the presence of sufficient hydrogen ions to solubilize Al and/or Fe from amorphous Al-Fe-Si compounds in the sediment, thus releasing amorphous SiO₂. Wilding *et al.* (1977) reported that the sorption of Al or Fe onto amorphous SiO₂ will decrease SiO₂ dissolution, but that such coatings decrease as the pH decreases resulting in an increase in silica dissolution.

The rapidly increasing Si and Al concentrations in the N₂ atmosphere at 25°C may be attributed to increased reaction rates as a result of the temperature increase, high pH (8.4–9.3), or to the reduction and removal of

Table 4. Oxalate extractable iron content of clays equilibrated in the laboratory.

Length of equilibration (days)	Temperature (°C) ¹	C-Horizon clay (mg Fe/g clay)			A-Horizon clay ² (mg Fe/g clay)	
		N ₂	Air	CO ₂	N ₂	Air
14	4	1.2	1.4	1.4	4.6	3.9
28	4	1.2	1.5	1.1	4.3	4.2
45	4	1.2	1.4	1.4	4.6	3.6
69	25	1.7	1.0	2.0	6.6	4.1
85	25	1.2	1.3	1.9	6.4	5.0
98	25	1.4	1.2	2.4	8.0	5.4
Reference ³		1.1			3.8	

¹ After 45 days, the temperature was increased from 4°C to 25°C.

² A-horizon clays were not equilibrated in CO₂ atmospheres.

³ Reference value, obtained prior to equilibration.

iron coatings from aluminosilicate surfaces as reducing conditions became more intense. Removal of such coatings would expose the surfaces to dissolution. The high pH in the N₂ atmosphere is perhaps related to the production of ammonia, and the release of hydroxyl ions following the reduction of ferric and manganic compounds at low redox potentials (Redman and Patrick, 1965).

Fe concentrations in solution at 4°C were low, with minimal differences between treatments. At 25°C, the N₂ atmosphere effected a substantial increase in soluble iron; whereas, concentration changes in the CO₂ and air atmospheres were slight and approximately equal (Figure 3). The differences in the Fe concentration of equilibrating systems appear to be strictly related to redox potential. Low redox potentials in the N₂ system led to the reduction of the oxidized zone at the sediment-water interface permitting a greater concentration of ferrous iron to diffuse through into solution. The processes were greatly affected by the change in temperature since comparable redox potentials were recorded at both temperatures but much higher concentrations existed at 25°C.

Mn concentrations in solution at 4°C were erratic with essentially none being detected in any system other than the CO₂-equilibrated system. The CO₂ system also yielded the highest concentrations at 25°C but substantial amounts were also recorded in the N₂ system. No detectable Mn was found in the air-equilibrated system at 25°C. The results suggest that Mn in solution is controlled more by pH than by redox potential. Gotoh and Patrick (1972) reported similar findings; however, they found that a pH of 5 was required for the Mn solubility to be relatively independent of redox potential.

Concentrations of Ca and K in solution followed the general order CO₂ > air > N₂, but showed no trends with time other than a slight increase in Ca in the solution equilibrated in CO₂. The Ca concentrations may have been controlled by the dissolution of calcite and/or dolomite in the sediments because the highest concentrations were associated with the lowest pH values. Even though carbonate dissolution was not evident for clays equilibrated in the laboratory, carbonate dissolution was noted for clays equilibrated in the river.

CONCLUSIONS

Clay mineral alterations were minimal when equilibrated for 217 days in a freshwater bottom sediment environment. The only significant changes were a decrease in total Al and Si, a dissolution of carbonates, a possible reduction in particle size as indicated by XRD peak broadening, and an increase in surface area; however, basal spacings remained unchanged. In laboratory equilibrations, few significant changes occurred other than an increase in the oxalate-extractable iron content of clays. This study provides little support

for substantial clay mineral alterations during residence in the Maumee River drainage system; thus mineralogical differences between soils in the watershed and sediments in this drainage system are attributed primarily to preferential transport.

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Резюме—Чтобы распознать минеральные преобразования, которые могут произойти в среде потока, преимущественно иллитовые почвенные глины были уравновешены в среде донных отложений в естественных и лабораторных условиях на протяжении 217 и 98 дней соответственно. Изменения, происшедшие после 217 дней на дне реки Оглаз включали уменьшение содержания карбоната, уменьшение размеров зерен и небольшие потери Al и Si; однако не было обнаружено существенных изменений в базальных промежутках.

Глины, уравновешенные в речной воде в лабораторных условиях при 4° и 25°C в CO₂, N₂, или воздушной атмосфере, показали только увеличение содержания железа, извлекаемого оксалатом. Концентрации Al, Si, Fe, Mn, K, и Ca в растворе над глинами изменялись в зависимости от атмосферы и температуры. Растворение аморфных соединений Al–Fe–Si возможно повлияло на концентрацию Fe, Al, и Si в растворе. Следовательно, минералогические различия между почвами в бассейне реки и осадками в дренажной системе не могут быть обусловлены минералогическим преобразованием во время пребывания в дренажных системах. [N.R.]

Resümee—Um Mineralumwandlungen zu bestimmen, die in Flußmilieus auftreten können, wurden überwiegend illitische Bodentone in Bodensedimenten unter natürlichen und Labor-Bedingungen für 217 bzw. 98 Tage ins Gleichgewicht gebracht. Die Veränderungen, die nach 217 Tagen auf dem Grund des Auglaize-Flusses auftraten, bestanden in einer Abnahme des Karbonatgehaltes, einer Verkleinerung der Teilchengröße und einem geringen Verlust von Al und Si. Es wurden jedoch keine bemerkenswerten Veränderungen bei den Basisabständen beobachtet.

Tone, die unter Laborbedingungen bei 4° und 25°C in Flußwasser bei CO₂-, N₂-, und Luft-Atmosphäre ins Gleichgewicht gebracht wurden, zeigen nur eine Zunahme des durch Oxalat extrahierbaren Eisens. Die Konzentrationen von Al, Si, Fe, Mn, K, und Ca in der Lösung über den Tonen variiert mit der Art der Atmosphäre und mit der Temperatur. Die Konzentrationen an Fe, Al, und Si in der Lösung könnten durch die Auflösung amorpher Al-Fe-Si-Komponenten beeinflusst werden. Deshalb können die mineralogischen Unterschiede zwischen den Böden im Einzugsgebiet und den Sedimenten im Entwässerungssystem nicht auf mineralogische Veränderungen während des Aufenthalts im Entwässerungssystem zurückgeführt werden. [U.W.]

Résumé—Pour identifier les altérations minérales qui se produisent dans des environnements fluviaux, des argiles de sol predominantement illitiques ont été équilibrées dans des environnements de sédiments de lit sous des conditions naturelles et de laboratoire pendant respectivement 217 et 98 jours. Les changements qui se sont produits après 217 jours dans le lit de la rivière Auglaize consistaient en une réduction en contenu en carbonate, en une diminution de la taille de particule, et en une légère perte d'Al et Si; aucun changement significatif n'a cependant été observé dans les espacements de base.

Les argiles équilibrées dans l'eau de rivière sous des conditions de laboratoire à 4° et 25°C dans des atmosphères CO₂, N₂, ou l'air n'ont montré qu'un accroissement en fer à oxalate qui peut être extrait. Les concentrations en Al, Si, Fe, Mn, K, et Ca en solution au dessus des argiles variaient selon l'atmosphère et la température. Les concentrations en Fe, Al, et Si en solution peuvent avoir été influencées par la dissolution de composés Al-Fe-Si amorphes. Les différences minéralogiques entre les argiles dans la ligne de partage des eaux et dans les sédiments du système de drainage ne peuvent donc pas être attribuées à des transformations minéralogiques se produisant pendant la résidence dans le système de drainage. [D.J.]