

Characterization of the Pembroke Soils from Indiana¹

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Abstract

Pembroke soils which have developed from high grade calcitic limestone, capped with a shallow loess overburden, were studied to determine changes in clay mineral composition and soil properties which occurred in the soil profile. Analysis showed a major clay mineral transformation from an illitic type in the parent rock to a mixed suite of clay minerals including a significant quantity of kaolinite. Special consideration is given to the genesis of the clay minerals.

The well drained Pembroke soils have weathered from high grade Mississippian age limestone. The solum is usually 40-100 inches thick and commonly has a thin (less than 18 inches thick) loess mantle. These soils occur in south-central Indiana, General Soil Region M.

The Pembroke soils of this study would be classified as a member of the fine, kaolinitic, mesic family of the Ultic Hapludalfs.³ Under the 1938 soil classification system this soil was classified in the Red-Yellow Podzolic great soil group.

The Pembroke sites were sampled and designated as Pembroke I and II. The results from the two sites were very similar and therefore only the results for the Pembroke II site will be presented. Refer to Post (4) for the complete analyses of both sites. The following is the detailed profile description of Pembroke II:

Location: NW 1/4 of SE 1/4 Sec. 21, TIN, R2E; Madison Twp. Washington County, Indiana.

Vegetation: Grass and second growth shrubs and cedars.

Parent Material: High grade Mississippian age limestone, St. Genevieve Formation, with a shallow loess overburden.

Slope: 11%

Permeability: Moderate.

Drainage: Well (IV).

Comments: This soil was sampled from a brush covered site on the east side of a gravel road. The loess overburden is 17 inches thick and the 13-17" B21t appears to be a transitional horizon. The B21t has a distinct accumulation of coarse cherty and high iron rock fragments, suggestive of a former land surface.

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³There is some question yet as to the final classification of this series. It is listed in the Classification of the Northeastern (Region) Soil Series, July 1967 as a member of a fine silty mixed mesic family of Ultic Paleudalfs. This research was supported in part by National Science Foundation Grant GP-1219.

A1 0-2": Brown (10YR 5/3 moist, pale brown (10YR 6/3) dry, silt loam; moderate medium granular structure; friable; many fibrous grass roots; mildly alkaline; abrupt smooth boundary.

A2 2-9": Light yellowish brown (10YR 6/4) moist, very pale brown (10 YR 7/4) dry, silt loam; moderate medium granular and very weak platy structure; friable; medium acid; clear smooth boundary.

Blt 9-13": Yellowish red (5 YR 4/6) moist, reddish yellow (10 YR 6/6-6/7) dry, heavy silt loam; moderate fine and medium subangular blocky structure; friable to slightly firm; very strongly acid; clear smooth boundary.

B21t 13-17": Yellowish red (5YR 4/6) moist, yellowish red (5YR 5/8) dry, clay loam; moderate medium subangular blocky structure; friable to slightly firm; high proportion of coarse material present; very strongly acid; clear smooth boundary.

II B22t 17-28": Dark red (2.5YR 3/6) moist, red (2.5YR 4/6) dry, clay; moderate medium and coarse angular blocky structure; firm; common clay skins; very strongly acid; gradual smooth boundary.

II B23t 28-54": Dark red (2.5YR 3/6) upper horizon grading to red (2.5YR 4/6) dry, clay; moderate coarse angular blocky structure; very firm; common yellowish red (5YR 4/6) clay skins becoming thicker and more numerous with depth; few Fe-Mn concretions in lower part of this horizon; very strongly acid; abrupt; smooth boundary.

II B3-C 54-54.5": Dark reddish brown (5YR 3/4) moist, reddish brown (5YR 4/3-4/4) dry, clay; massive; very firm; many white and gray highly weathered, calcareous limestone fragments; pH of the B3 material is slightly acid to neutral; abrupt smooth boundary.

II R 54.5" +: High grade calcitic limestone.

Table 1 gives the mechanical analyses and pH data for the Pembroke soils. The thick II B23t, 28-54 inch horizon, was subdivided for laboratory analyses.

The Roman Numeral prefix II was used in the field to denote the break between silty textured, brown to yellowish red colored loess overburden and the clayey textured, reddish color of the limestone residuum. The mechanical analyses results in table 1 clearly support the field observation of this parent material break. The B21t horizon is a transition horizon with 37.6% clay as compared to 26.9% in the B1t horizon and 60.4% in the II B22t horizon.

A detailed study was made to characterize the types of clay found in this soil. The clay was fractionated into two size groups, 2.0-0.2 μ , and a detailed x-ray analyses was made. Selected x-ray tracings for the 2.0-0.2 μ fraction are presented in Figure 1.

The most significant feature of these treatments is the variable 14.2 to about 17 Å spacings of the vermiculite-montmorillonite type clays, and in certain horizons, the resistance to collapse to 14.2 Å with K-saturation and mild heat treatment. The variable expansion characteristics is a function of the variable layer charge of this fraction. Post and White (4) have discussed this in greater detail. The resistance

TABLE 1
Mechanical analyses and pH data for the Pembroke soils

Horizon	Depth in Inches	pH	Total Sand (2.0-.05 mm)	Total Silt (.05-.002 mm)	Fine Silt (.02-.002 mm)	Total Clay ($< 2.0\mu$)	Total Clay ($< 0.2\mu$)
A1	0-2	7.5	17.0	66.4	44	16.6	5.8
A2	2-9	5.7	16.8	65.4	43	17.8	8.3
B1t	9-13	4.6	15.7	57.4	39	26.9	13.9
B21t*	13-17	4.6	21.7	40.7	28	37.6	24.0
II B22t	17-28	4.8	14.2	25.4	17	60.4	45.1
II B23t	28-36	4.6	18.0	17.4	11	64.6	51.4
II B23t	36-42	4.7	20.4	16.9	11	62.7	49.4
II B23t	42-48	4.7	15.4	15.4	10	69.2	53.6
II B23t	48-54	4.9	11.5	21.9	13	66.6	49.5
II B3-c	54-54.5	6.8	6.5	16.9	9	77.1	56.1
II R†			16.7	31.1	12	52.2	10.0

* 21% by weight—2.0 mm coarse skeletal material.

† Analyses of the impurities within the rock.

to collapse, most pronounced in the upper loess derived horizons and lowest residuum horizons, suggests the presence of hydroxy aluminum interlayers.

It is often important to estimate the clay components and these results are included in Table 2. (The problem of quantifying the clay minerals in soil clays is discussed by Post and White (5) in the same issue of these proceedings).

Summary and Conclusions

Physical, chemical, and mineralogical characterization of the limestone-derived Pembroke soils showed them to be very clayey, highly acidic, and highly oxidized soil profiles. The laboratory results supported field observations that these soils have a shallow overburden of loess. The following points relative to the mineralogical composition of the solum should be noted:

1. The kaolinite content was high in the residuum horizons.
2. Large amounts of quartz and/or amorphous materials were present in the upper solum horizons.
3. Vermiculite was highest, as was kaolinite, in the residuum horizons.
4. Montmorillonite occurred only in the loess derived horizons and the lowest residuum horizons.
5. Mica remained relatively constant throughout the solum.
6. Evidence for some interstratification was noted.
7. Significant amounts of interlayering, presumably hydroxy-aluminum interlayers, occurred in the loess horizons and lowest residuum horizons.

The presence of a shallow loess deposit necessitates the evaluation of two weathering regimes to determine the genesis of the clay in this soil.

It was impossible to determine the nature and properties of the parent clay minerals in the loess prior to weathering. However a detailed characterization was made of the clay minerals occurring in the insoluble residue from the limestone parent rock.

The total composition of the insoluble residue shows mainly illite present in the $< 2.0\mu$ fraction with quartz and illite present in the $> 2.0\mu$ fraction. With this high percentage of illite and the general illitic nature of limestone residues, it follows that illite is the primary parent mineral of the Pembroke clay.

Results of x-ray diffraction showed an abrupt transformation from illite in the parent rock insoluble residue to a mixed clay mineral suite of kaolinite, vermiculite, mica, and montmorillonite. The abrupt change is attributed to the presence of some readily weathered illite inherited from the parent rock and the time factor which is thought to be quite long. A comparison of the illite 10 A/5A peak height ratio and layer charge density measurements indicates the illite in the parent rock has a lower K content and possibly some iron in lattice coordination. This low K content illite weathers first, leaving a mica-type mineral which persists in the solum.

Horizon	Depth	% Mica ¹	% Kaolinite ²	% Vermiculite ³	% Mont- morillonite ³	% Quartz, Fe ₂ O ₃ and/or amorphous materials ⁴
			2.0-0.2 μ			
A1	0-2	14	24	17	—	45
A2	2-9	14	21	15	—	50
B1t	9-13	16	28	14	2	40
B21t	13-17	10	35	15	3	37
II B22t	17-28	8	46	20	4	22
II B23t	28-36	7	51	24	—	18
II B23t	36-42	9	53	25	—	13
II B23t	42-48	10	49	24	—	17
II B23t	48-54	8	51	25	5	11
II B3-C	54-54.5	16	30	27	5	22
			< 0.2 μ			
A1	0-2	8	29	10	20	33
A2	2-9	7	30	15	15	33
B1t	9-13	11	39	26	5	19
B21t	13-17	9	45	31	5	10
II B22t	17-28	8	40	32	—	20
II B23t	28-36	9	48	29	—	14
II B23t	36-42	8	50	32	—	10
II 23t	42-48	12	47	32	—	9
II B23t	48-54	11	42	36	—	11
II B3-C	54-54.5	9	33	32	—	26
			> 2.0 μ			
II R		59	—	9	1	31

Percentages estimated as follows: ¹ % K₂O $\times$ 10 after dissolving in HF. ² Average of peak and DTA values compared to prepared standards. ³ Specific surface and peak height. ⁴ 100% minus total of crystalline clay minerals.

Barshad (1), after an extensive survey of the colloids in soils, concluded that the chemical environment which exists during soil development determines the kind of clay minerals that are being formed. This is particularly true of limestone soils where the initial stage of soil formation consists of the accumulation of residues through dissolution of the carbonate rock. It is often easy to characterize the macro-environment, but truly the heterogeneous micro-environment of the carbonic acid-carbonate rock-subsequent soil residue should be considered. Particular consideration must be given to the abnormal surface acidity of the colloidal clay.

The occurrence of interlayering in clays has been reported by many workers. Jackson (2) recognized this and has incorporated it as a part of chemical weathering sequences. Interlayering, thought to be predominately of the hydroxy-aluminum type, was very prevalent in the soil-rock contact sample and also in the upper loess-derived horizons. The nature and properties of this interlayer material are very important to a complete understanding and interpretation of the Pembroke clay genesis. Montmorillonite was noted in the same horizons where the interlayer material was most prevalent.

It is concluded from this study that nearly identical weathering sequences are occurring in the upper solum horizons and at the soil-rock contact. The general weathering sequence is as suggested by Jackson (2). However the time factor is quite different for these two regimes and therefore the clay mineral composition varies.

In brief the following sequence of reactions are thought to occur.

As illite weathering progresses, potassium and other interlayer cations slowly diffuse out of the interlayer spaces. This can occur on the edges of the mica flakes where only the edge of the main flake will expand. This is referred to as "frayed-edge" type of interlayering. However it is possible that any given mica interlayer segment may tend to remain completely filled with K or else to become completely affected by interlayer swelling. This can be depicted as follows:



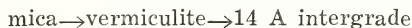
It is easy to see that interstratification would result if random expansion occurs in a mica flake. This is very widespread in soils and sediments.

The sequence of a non-expandable 2:1 mineral (mica) weathering to a partially expandable 2:1 mineral (illite) weathering to a freely expandable 2:1 mineral (vermiculite or montmorillonite), as indicated above, is shown in most weathering sequences. This implies a lowering of the layer charge. In soils there is a gradation between dioctahedral vermiculite and dioctahedral montmorillonite and variable-charge expandable 2:1 minerals are found. It would seem that a low-charge vermiculite may characteristically be very similar to a high-charge montmorillonite. Therefore the significance of montmorillonite in the sequence may be open to question.

The next step, which appears to be a characteristic function of chemical weathering in soils (2), is that of intercalation of hydroxy-alumina interlayers in the expanded 2:1 layer silicates. Not only can this

hydroxy-alumina interlayer be attached on the two interlayer surfaces of vermiculite, but it can precipitate on one interlayer surface of an expanded montmorillonite. A montmorillonite intergrade appears to form frequently in alkaline soils whereas a vermiculite intergrade is more common in acid soils.

The reaction



is favored by relatively rapid decomposition of any montmorillonite formed because of higher specific surface of edges, with release of aluminum for formation of hydroxy-alumina interlayers in the more highly charged and larger vermiculite particles forming from mica. This disposition of aluminum tends to preclude free $\text{Al}(\text{OH})_3$ (gibbsite) formation so long as there are actively weathering 2:1 layer silicates present. This weathering then proceeds as follows:



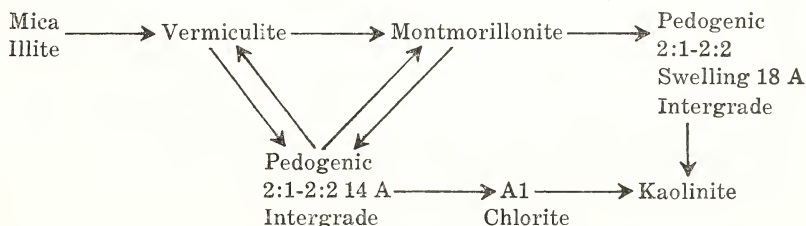
It is thought that as weathering progresses the 2:1-2:1 intergrade accumulates aluminum in acid soils to a point where the transformation to a 1:1 occurs. The true nature of this transformation is not known.

This final kaolin product can perhaps be visualized as being formed in the outermost parts of the mica plates, the "frayed edges," and progressing along the original cleavage expansion plane. The skeleton of weathered minerals can serve as a concentrated source of silica and alumina, but all progress through a solution phase or surface migration to give rearrangement of ions.

The presence of much vermiculite in the residual horizons is due to the weathering and expansion of the dioctahedral mica in the limestone. The decomposition of montmorillonite was noted earlier as the source of alumina for interlayer development. This could be the controlling step in this process.

The reason montmorillonite occurs in certain horizons is that the formation of montmorillonite is promoted by a higher pH which exists at the rock contact. The pH is also higher in the upper horizons due to cycling of bases by the vegetation. However the montmorillonite in the upper horizons could be simply inherited from the loess.

These reactions can be summarized as follows (2):



The intense red color and clayey character of limestone soils are functions: (1) of the inherited parent material, and (2) of the time factor, which appears to be great. Mechanical analyses of the parent rock insoluble residue showed $50\% < 2.0\mu$ in size. It seems the iron is in the parent rock as discrete iron compounds segregated in the rock, and

when freed, remain as inert iron oxide in the soil. It is possible iron may be coating the surfaces of the clay minerals.

The fact that the Pembroke soil is well drained is envisioned as promoting the weathering reactions which have occurred.

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