

Recognition and chemical characterization of fossil soils developed on alluvium; A Late Ordovician example

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ABSTRACT

Fossil soils in alluvial red beds from the Juniata Formation, near Potters Mills, in central Pennsylvania, provide evidence of soil-forming processes during Late Ordovician time. Paleogeographic and facies considerations indicate that the fossil soils formed on flood plains west of the Taconic uplift.

Most studies of paleosols of this age or older have considered soils developed on metamorphic or igneous basement rock. Alluvial fossil soils provide evidence of conditions during shorter intervals of weathering without problems of overprinting by successive and different weathering regimes. They can be recognized by the presence of trace fossils and the development of soil horizons and structures. Problems associated with such fossil soils include establishing the nature of the parent material and distinguishing clay formation in the soil from originally deposited fining-upward cycles.

These difficulties can be overcome by comparing paleosols in different stages of development, as indicated by degree of ferruginization, density of trace fossils, amount of clay, and abundance and size of caliche nodules. In modern soils, caliche forms in alkaline conditions under which TiO_2 is stable. Gains and losses of oxides (measured in grams per cubic centimeters) relative to TiO_2 in a strongly developed paleosol were compared with those of a weakly developed paleosol, taken to approximate the compositional range of the parent material. Concentration ratios indicate significant soil development of the strongly developed paleosol beyond the compositional range of the weakly developed paleosol. There was depletion of SiO_2 and enrichment of Fe_2O_3 , Al_2O_3 , and K_2O relative to TiO_2 . Anomalous enrichment of K_2O has been documented in other fossil soils. Both x-ray diffraction studies and a strong correlation between K_2O and Al_2O_3 are evidence that most of the potassium is contained in sericitized illite.

INTRODUCTION

Identification of Tertiary and Quaternary paleosols is usually straightforward because of their distinctive root traces, profile development, color, and mineralogical variations. Yet paleosols older than Silurian are much more difficult to recognize, especially within alluvial sequences. In large part this is because vascular land plants were not yet available to stabilize, bioturbate,

and chemically alter the land surfaces. This chapter provides a detailed description of Late Ordovician soil development on alluvial parent materials. Because little evidence of plant activity is apparent in these paleosols, evaluation of soil formation is based primarily on chemical analyses and on the study of trace fossils.

Early Paleozoic and Precambrian paleosols developed on

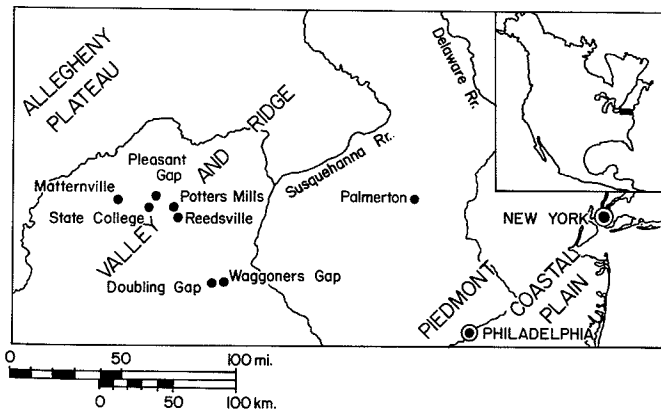


Figure 1. Location of Potters Mills, and other mentioned localities in Pennsylvania.

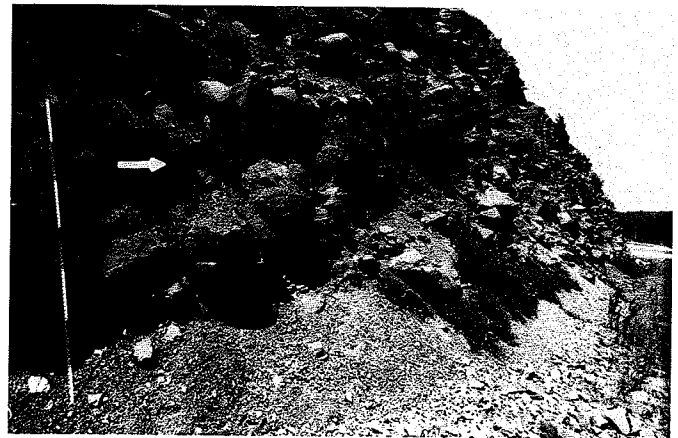


Figure 2. Roadcut, 4.2 km southeast of Potters Mills. Arrow indicates the top of Potters Mills clay. Scale on left is in feet.

unconformities between igneous or metamorphic basement rocks and overlying sediments are easy to recognize and are now studied using a variety of geochemical approaches (Holland, 1984; Retallack, 1986a; Retallack and others, 1984). Yet these paleosols are difficult to understand because they have been subjected to several cycles of weathering during their long exposure. This study seeks to apply comparable methods of paleopedological analysis to paleosols developed within ancient alluvium. A vexing problem in analysis of such paleosols is the identification of a uniform parent material. Both fining-upward cycles and inter-layered shaly and sandy beds characteristic of alluvium could be confused for soil horizons if partly bioturbated. In addition, in well-indurated rocks it is very difficult to distinguish clays and micas originally present from those produced by soil formation, and then by late diagenesis and metamorphism. Despite these difficulties, paleosols developed on alluvial lowlands may provide more reliable paleoenvironmental information than paleosols, which formed at major geologic unconformities.

LOCATION AND GEOLOGICAL SETTING

The Juniata Formation is one of several red beds of Paleozoic age exposed in the Valley and Ridge Province of the Appalachian orogen (Meckel, 1970). It is Late Ordovician (Ashgillian, or 438 to 448 Ma) in age (Ross, 1982). Paleosols in the Juniata Formation are especially well exposed within a roadcut 4.2 km southeast of Potters Mills along U.S. 322, in Center County, Pennsylvania (Figs. 1, 2). The type profile of the Potters Mills clay paleosol (Retallack, 1985) overlies the type Faust Flat silty clay paleosol (named here) 200 m east of the western end of the southern cutting, at a stratigraphic level of 75 to 76 m (245–250 ft) in a measured section with its base at the western end of the roadcut (Fig. 3). There are numerous other Potters Mills and Faust Flat Series paleosols in this sequence.

This part of Pennsylvania was removed from the regions of intense metamorphism and structural deformation due to Appalachian mountain building. The outcrops examined are folded into a shallow, asymmetrical syncline that plunges gently to the west-southwest (Fig. 2). The degree of alteration of conodonts in Ordovician limestones of Pennsylvania and the illitic and chloritic composition of the Juniata paleosols are compatible with lower greenschist facies burial metamorphism. The Potters Mills clay and the Faust Flat silty clay appear to have escaped intense structural or metamorphic alteration (Retallack, 1985).

Fossil soils of the upper Juniata Formation are within alluvial red beds that are part of a large wedge of clastic sediments derived from the Taconic uplift to the southeast (Thompson, 1970a). Cross-bedding, maximum pebble size, and isopach data, along with the lack of marine fauna and the presence of mud-cracks and ripple marks, are evidence that this part of the clastic wedge was nonmarine. Fining-upward sequences of red-maroon sandstones and shales within this part of the Juniata Formation were deposited by loosely sinuous streams that drained the ancestral Appalachian highlands (Thompson, 1970b). Marine rocks of comparable age are 260 km northwest of these paleosols in the Juniata Formation (Yeakel, 1962). Thus, the paleosols reported here formed on inland portions of a coastal plain.

DESCRIPTION AND INTERPRETATIONS OF THE PALEOSOLS

Potters Mills clay paleosol

Diagnosis. Thin (42 cm in compacted paleosol), clayey to silty, dark reddish brown (2.5YR3/4) to weak red (2.5YR4/2) paleosol, containing numerous subhorizontal and vertical burrows (Fig. 4), half of which are encased or closely associated with caliche nodules (Fig. 5).

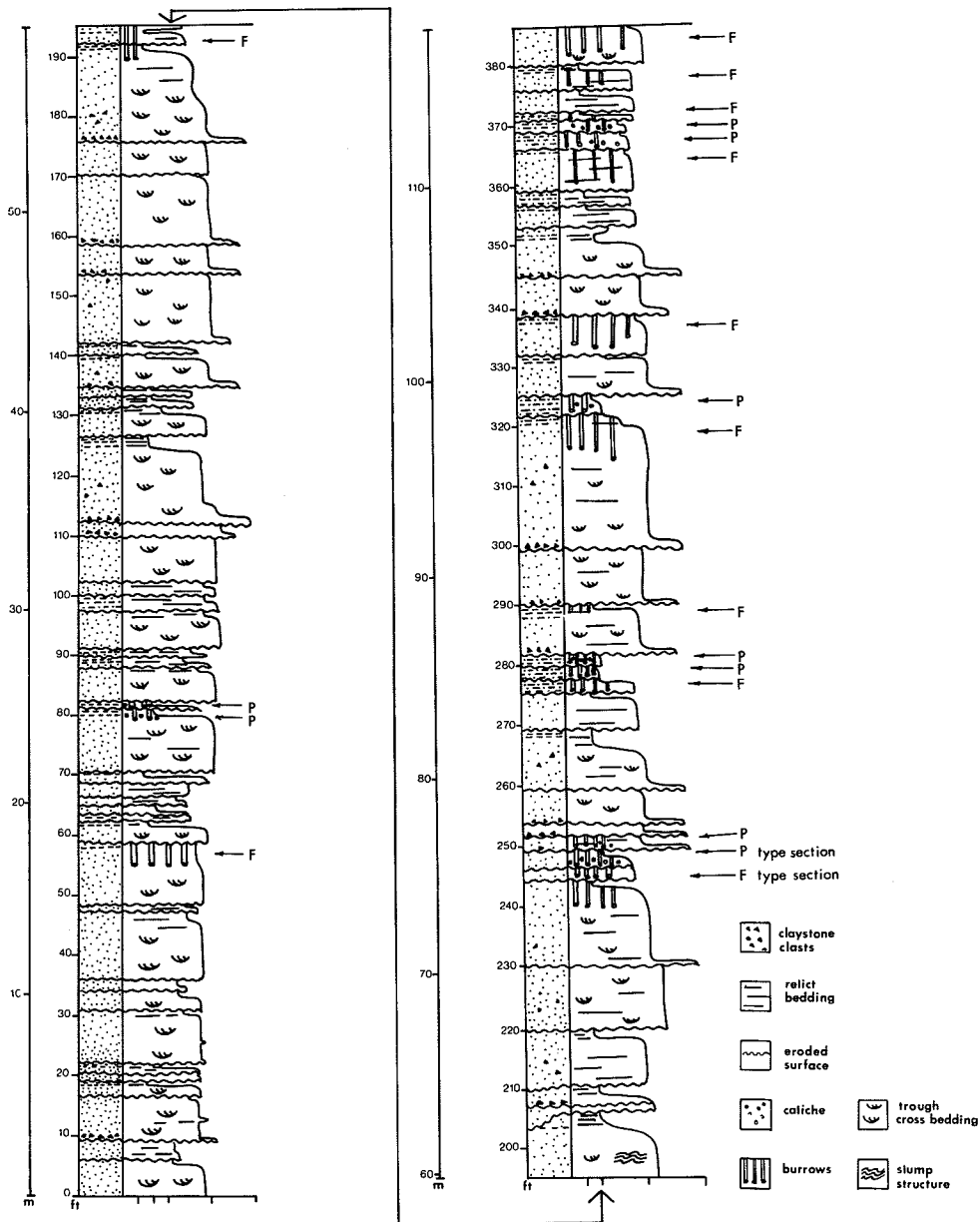


Figure 3. Columnar section of paleosols within the Upper Juniata Formation. P indicates Potter Mills Series paleosols; F indicates Faust Flat Series paleosols.

Derivation. Potters Mills is a small village in Pennsylvania, 4.2 km northwest of the type profile.

Description. In the following descriptions, measurements are from the top of the profile to the top of the described horizon, and the letters are their interpretation as a soil horizon, following the labeling scheme of Birkeland (1984). Unlike earlier schemes of nomenclature (used by Retallack, 1985), this scheme treats calcic horizons as B rather than C horizons. The micromorphological terminology is that of Brewer (1976).

+24 cm Bk of overlying paleosol and base of overlying

sedimentary unit; silty claystone; dark reddish brown (2.5YR3/4); weakly calcareous; prominent relict bedding; few, medium (3 to 15 mm) diffuse burrow-sheathing and fine, tubular calcareous nodules of reddish yellow (7.5YR7/2) with reddish brown (5YR5/4) neosequans; microtexture unistrial, agglomeroplasmic skelinsepic, mainly clay and quartz, with conspicuous mica, rare calcite, and rock fragments; common medium diffuse irregular sesquioxidic nodules and stain, locally isotropic abrupt wavy contact to

0 cm, A, claystone; dark reddish brown (2.5YR3/4); cal-



Figure 4. Subhorizontal burrows from A horizon of Potters Mills clay. Scale is 1 inch.

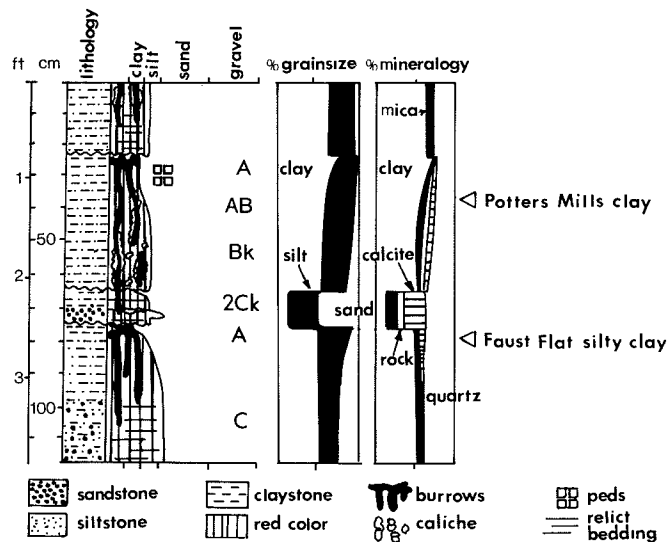


Figure 5. Columnar section (measured in field) and petrographic composition (from point counting of thin sections) of Potters Mills clay paleosol and Faust Flat silty clay paleosol, Late Ordovician, central Pennsylvania. Letters indicate soil horizons.

careous; medium to coarse (3 to 4 cm) subangular blocky peds defined by abundant subhorizontal and vertical, 1 to 15 mm diameter para-aggotubules, and in some areas by few, very dark grayish brown (10YR3/2) neomangans; these structures impart a hackly appearance to the rock except for relict bedding (presumably cumulic) nearest the surface; few medium, irregular, diffuse mottles of greenish gray (5GY5/1) claystone, presumably around relict organic matter; microtexture unistrial, agglomeroplasmic,

skelmosepic, mainly clay with conspicuous quartz, lesser mica and rare calcite; common diffuse sesquioxidic nodules, especially along relict clayey laminae; gradual smooth contact to

-8 cm, AB, silty claystone; weak red (2.5YR4/2); calcareous; weak structure of medium (3 to 4 cm) subangular, blocky peds, defined by abundant vertical, dark reddish brown (2.5YR3/4), 2 to 15 mm diameter para-aggotubules, some of which are sheathed with a thin inner reddish brown (7.5YR7/6) neosesquan and thicker (1 to 2 mm) outer quasi-calcitan which imparts a light color to the surface of the trace; structure also defined in places by few, very dark grayish brown (10YR3/2) neomangans; microtexture unistrial, agglomeroplasmic, skelinsepic to inundulic; mainly clay with common quartz, little mica and calcite, rare feldspar and rock fragments; microstructure of the para-aggotubules skelinsepic; common diffuse irregular sesquioxidic nodules, isotic in places; gradual smooth contact to

-19 cm, Bk; silty claystone; weak red (2.5YR4/2); calcareous; faint relict bedding; common dark reddish brown (2.5YR3/4), vertical para-aggotubules, sheathed with inner reddish brown (5RY5/4) neosesquan and outer reddish yellow (7.5YR7/6) quasicalcitan; few, small (1 to 3 mm in diameter), calcareous crystal tubes; calcareous aggregations confined largely to this horizon, but patchily distributed on the scale of tens of centimeters over the 100 m of lateral exposure examined; one burrow found retains some clayey fill as a neoargillan around a central ortho-granotubule; a few vertical parastriotubules exhibit spreiten texture; few medium, drab, greenish gray (5GY5/1), subhorizontal mottles near the base of this horizon, presumably after relict organic matter; microstructure unistrial, agglomeroplasmic, argillasepic to skelinsepic; mainly clay with abundant quartz, common calcite and mica, rare rock fragments and feldspar; few irregular diffuse sesquioxide nodules and stain; abrupt planar contact to

-32 cm; 2Ck; silty claystone; with shale laminae in upper part; weak red (2.5YR4/2); calcareous; a disrupted, 2 cm thick, medium-grained sandstone bed in the central part of this horizon is light yellowish brown (2.5Y6/4) with some drab mottles of greenish gray (5GY5/1) along its upper surface; much relict bedding and few para-aggotubules like those in overlying horizons; microtexture intertextic silasepic and cristic, with laminae and clots (after clasts or rock fragments) of more clayey, porphyroskelic argillasepic texture; mainly quartz in a matrix of calcareous or chloritic clay and clear carbonate, common rock fragments and mica; few diffuse irregular isotic sesquioxidic nodules; locally abrupt wavy contact to A horizon of underlying Faust Flat silty clay paleosol.

Reconstructed soil. This paleosol is most similar to alluvial bottomland soils of the seasonally dry tropics, and has been identified as an Oxic Ustropept (USDA classification), Calcic Cambisol (FAO) and Calcareous Red Earth (CSIRO): with some trepidation considering likely differences in degree and kind of soil-forming processes during Late Ordovician time (Retallack, 1985).

The present paleosol is stained red by hematite, but the

original soil color may have been orange or brown from more hydrated ferric oxyhydrate minerals (Walker, 1967). The degree of calcification and ferruginization indicates alkaline and oxidizing conditions following general models of Retallack (1984). In modern strongly seasonal climates, carbonate accumulations may form during dry periods and ferruginization during wet seasons (Duchafour, 1982). These two processes and the mild alignment of the clay minerals (skelinsepic and skelmosepic agglomeroplastic fabric) are indicators of a well-drained soil. Using Arkley's (1963) and Jenny's (1980) studies of soils in modern arid climates, the depth of caliche indicates that the soil received less than 40 cm of rainfall annually. The degree of calcification is analogous to Stage I of Gile and others (1966), which formed in roughly 3,000 to 4,000 yr. Presumably, most of this carbonate was derived from windborne dust, as appears to be the case for calcareous soils today (McFadden and Tinsley, 1985). The calcareous cement in horizon 2Ck is distinct from the caliche, however, and most similar to ground-water calcretes as described elsewhere by Netterberg (1969) and Mann and Horowitz (1979). Thus the water table may have been intermittently at 50 cm below the compacted paleosol surface. Permanent waterlogging within the soil is unlikely, considering the absence of gley features, apart from a few drab mottles similar to those formed in other paleosols around buried organic matter (Retallack, 1983).

Abundant burrows provide evidence that soil fauna played a significant role in aerating the soil, clay production, and enhancing soil structure. The exact nature of these organisms is poorly known. Presumably they were arthropods and were sustained by some kind of nonvascular vegetation (Retallack, 1985).

Other examples. In addition to other Potters Mills Series paleosols seen in the roadcuts southeast of Potters Mills, similar paleosols have been seen in the Juniata Formation elsewhere in Pennsylvania (Retallack, 1985).

Faust Flat Silty Clay Paleosol (new name)

Diagnosis. Very thin (22 cm in compacted paleosol) dark reddish brown (2.5YR3/4) to weak red (2.5YR4/2) profile with thin clayey surface horizon, very weakly calcareous to noncalcareous, containing abundant burrows varying greatly in width (2 to 21 mm), and a sandy burrowed subsurface horizon (Fig. 5).

Derivation. Faust Flat is a broad valley immediately west of the roadcut containing the type profile.

Description. Conventions for this account are as for the preceding paleosol description.

0 cm, A, siltstone; weak red (2.5YR4/2); weakly calcareous; abundant subhorizontal and vertical, 1 to 21 mm diameter, dark reddish brown (2.5YR3/4) para-aggotubules; microtexture unistrial agglomeroplastic skelinsepic; mainly clay and quartz, common calcite and mica, some feldspar; few wispy irregular diffuse sesquioxidic nodules; gradual smooth contact to

–18 cm C; sandy siltstone; weak red (2.5YR4/2); noncalcareous; conspicuous relict bedding and few vertical para-aggotubules as in overlying horizon; microtexture unistrial

agglomeroplastic skelinsepic; mainly clay and quartz, with common mica, feldspar, and calcite, but few rock fragments; few diffuse irregular sesquioxidic nodules, with isotic texture in places.

Reconstructed soil. This paleosol may be identified as a Fluvent (USDA: Soil Survey Staff, 1975), Eutric Fluvisol (FAO: Fitzpatrick, 1980) or Alluvial Soil (CSIRO: Stace and others, 1968). Although very weakly calcareous, the base status of this soil is presumed to have been within the range of Eutric Fluvisols because amounts of MgO, CaO, Na₂O, and K₂O (Table 1) are comparable to those in the overlying calcareous Potters Mills clay paleosol.

As with the Potters Mills clay, its original color may have been less red. The degree of calcification is greatly reduced in this soil, probably because of a shorter time for formation (probably less than 1,000 yr, judging from data of Gile and others, 1966). The conspicuous relict bedding, very mild orientation of the clays (agglomeroplastic skelinsepic fabric), slightly reduced density of burrows, and small amount of clay in the A horizon also support the interpretation that this was a young soil. The burrows range from 2 to 21 mm in diameter, a much wider size range than observed in the Potters Mills clay. The biological significance of this difference is unclear, but we are continuing our investigation.

Other examples. Numerous other examples of Faust Flat Series paleosols were found in the roadcut southeast of Potters Mills (Fig. 2), as well as in association with Potters Mills Series paleosols in roadcuts on old highway 322 east of Reedsville (Retallack, 1985). Elsewhere in the Juniata Formation in Pennsylvania, especially in old roadcuts in which claystones are now heavily vegetated—for example, near Matternville, Waggoners Gap, Doubling Gap, and Pleasant Gap—Faust Flat Series paleosols are much more obvious than those of the Potters Mills Series. Several examples of Faust Flat Series paleosols can also be seen in the Late Silurian (Ludlovian) Bloomsburg Formation, near Palmerton, Pennsylvania. One of these, partly overprinted with caliche from an overlying paleosol, has been figured by Retallack (1985, Figs. 9, 15).

CHEMICAL COMPOSITION OF THE PALEOSOLS

In our attempt to assess quantitatively the amount of weathering these soil profiles have undergone, we have employed three approaches: (1) calculating the weight loss of the constituents from the profile, (2) comparing the variation in molecular ratios of selected oxides, and (3) normalizing each chemical component to a stable constituent to calculate concentration ratios. None of these methods is without drawbacks.

Concentration ratios are calculated on the assumption that a specific oxide—usually either TiO₂, SiO₂, or Al₂O₃—remains stable as weathering proceeds. Apparent gains and losses of other oxides can be compared with the presumed inert oxide. This method generally requires that the composition of the unweathered parent material is known and uniform: this is a serious problem for the Juniata paleosols because each paleosol devel-

TABLE 1. CHEMICAL COMPOSITION AND BULK DENSITY OF LATE ORDOVICIAN PALEOSOLS FROM THE JUNIATA FORMATION

Sample No.	Depth (cm)	Major Elements (weight percent)												Totals
		SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	MgO	CaO	Na ₂ O	K ₂ O	MnO	P ₂ O ₅	LOI	
169	P+11	62.59	1.05	16.17	4.79	2.76	3.00	0.54	0.09	4.46	0.19	0.046	3.68	99.37
170	P-1	62.14	1.07	16.39	6.49	1.69	2.82	0.49	<0.04	4.68	0.19	0.040	3.87	99.91
171	P-14	66.70	1.00	14.19	3.55	2.48	2.80	1.01	0.45	3.81	0.20	0.063	3.90	100.15
172	P-30	67.10	1.01	14.83	3.98	2.21	2.54	0.50	0.44	4.04	0.20	0.085	3.37	100.31
173	P-34	64.68	1.06	15.43	4.09	2.54	2.73	0.57	0.41	4.31	0.20	0.057	3.34	99.42
174	P-37	62.76	1.04	15.00	4.39	2.28	3.14	1.26	0.29	4.11	0.21	0.087	4.60	99.17
175	P-48	60.18	0.73	10.30	2.63	1.74	4.44	5.91	0.34	2.63	0.13	0.28	9.72	99.03
176	F-5	67.21	0.98	14.43	3.91	2.29	2.58	0.55	0.50	3.81	0.21	0.040	3.27	99.78
177	F-47	69.72	0.96	13.79	3.70	2.07	2.29	0.43	0.50	3.62	0.20	0.037	3.06	100.38

Sample No.	Depth (cm)	Trace Elements (ppm)												Bulk Density (gcm ⁻³)
		Ba	Co	Cu	Cr	Li	Nb	Ni	Sc	V	G	Zn	Zr	
169	P+11	355	21	<5	67	37	7	41	14.8	113	20	75	89	2.68
170	P-1	384	19	<5	67	25	<5	32	14.3	115	25	74	112	2.67
171	P-14	318	32	<5	58	33	11	35	12.8	92	28	64	112	2.70
172	P-30	358	34	<5	58	31	7	35	13.1	93	24	67	113	2.69
173	P-34	352	26	<5	60	32	6	33	13.4	97	27	67	119	2.66
174	P-37	361	20	<5	62	32	10	35	13.8	101	38	68	129	2.71
175	P-48	320	37	<5	42	28	15	25	10.7	66	44	---	87	2.64
176	F-5	316	29	5	59	37	16	38	12.7	94	29	66	186	2.71
177	F-47	306	20	13	54	36	17	36	11.9	85	30	61	247	2.65

Note: Depths are given in cm above (+) and below (-) the top of the type Potters Mills clay (P) and type Faust Flat silty clay (F) paleosols. Major and trace elements determined on a Baird PSI ICP and FeO from titration by Dr. A. J. Irving, University of Washington, Seattle; bulk density determined by weight difference in and out of water by C. F. Feakes, University of Oregon, Eugene.

oped on fining-upward sequences. This makes identification of a specific parent composition difficult. Well-developed paleosols can, however, be compared to the range of compositions seen in less well-developed paleosols.

For direct examination of the chemical variation within the soils, molecular ratios are more applicable to the Juniata paleosols. Using this approach, various combinations of oxides considered pedogenically significant are compared, and composition of the parent material is not a consideration.

Finally, calculation of weight gains and losses of constituents from the profile is based on the assumption of constant volume, which assumes minimal compaction of the profile due to the weight of the overlying sediment. In some paleosol soil studies (Retallack, 1986b), clastic dikes have been used to quantify the degree of compaction. In the Juniata paleosols, some compaction has occurred, as evidenced by partial flattening of the subhorizontal burrows. Assuming that these burrows were originally cylindrical, a crude compaction factor of 10 to 20 percent was calculated. The deformation of the horizontal burrows, however, varies greatly, and could have begun before burial of the paleosol, thus making quantitative estimates of compaction suspect. Compaction was not severe enough to affect noticeably the vertical and carbonate encrusted burrows. The ensuing calculations assume that compaction was negligible.

A suite of nine samples from the Juniata paleosols was analyzed for major and trace elements by ICP (inductively coupled argon plasma spectrometry) techniques at the University of Washington by Dr. A. Irving, who also determined values of FeO from potassium dichromate titration (Table 1). Bulk densities of the same samples were determined using standard methods. The range in density of these rocks was from 2.64 to 2.71 gm/cc (Table 1); the average density was 2.68 gm/cc. In general, the sandy C horizons are less dense than the clayey A horizons, which is probably because of the greater compaction of the A horizons.

Chemical variation

The variation of major oxides and of other elements has been plotted against columnar sections of the two paleosols (Figs. 6, 7). Disconformities at about 64 and 75 cm (Figs. 3, 4) represent abrupt changes in the composition of sediment originally deposited.

Sesquioxides and silica. The Potters Mills clay shows the most dramatic changes in sesquioxides and silica (Fig. 6). Iron and aluminum oxide increase by about 0.6 and 0.1 gm/cc, respectively, toward the top of the Potters Mills clay, whereas silica shows a corresponding decrease of about 0.2 gm/cc in the A

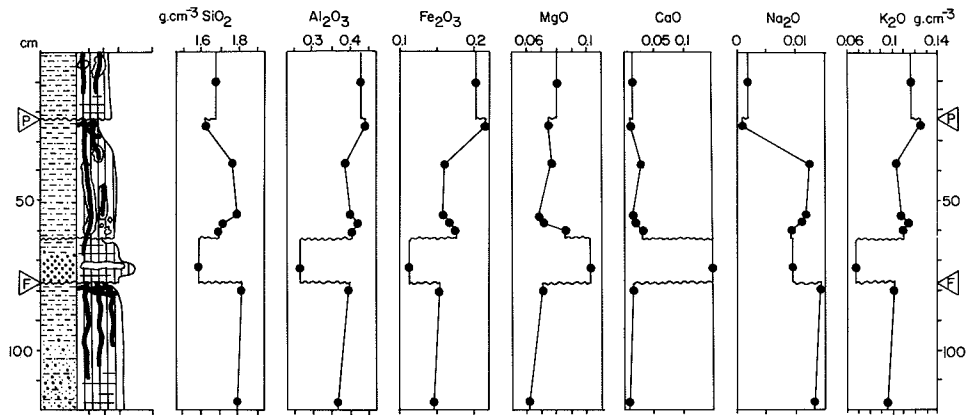


Figure 6. Variation in major oxides in Potters Mills clay (below upper triangle) and Faust Flat silty clay (below lower triangle) paleosols.

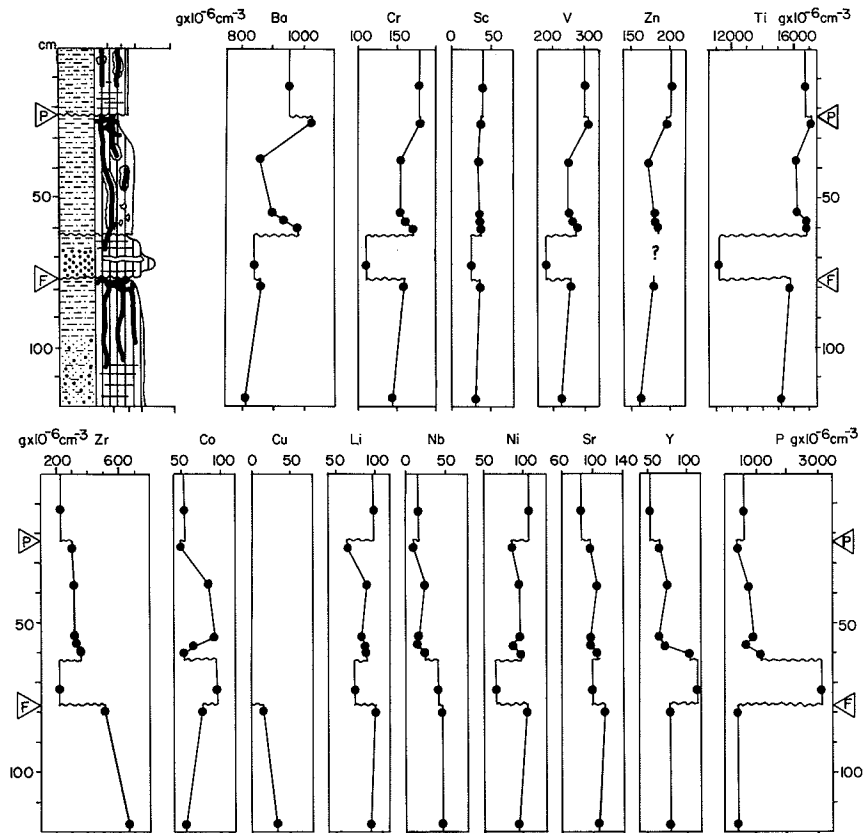


Figure 7. Variation in minor and trace elements in Potters Mills clay (below upper triangle) and Faust Flat silty clay (below lower triangle) paleosols.

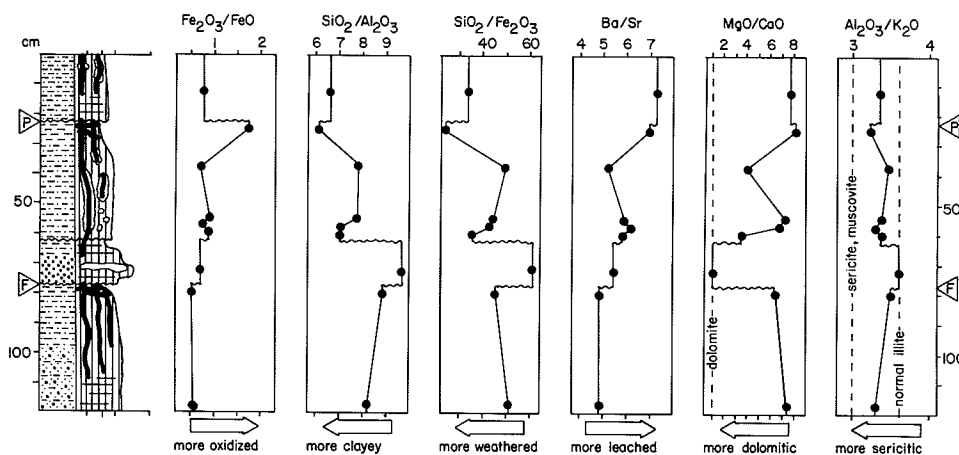


Figure 8. Selected molecular ratios (calculated in grams per cubic centimeter) chosen to illustrate degree of weathering and mineralogy of Potters Mills clay (below upper triangle) and Faust Flat silty clay (below lower triangle) paleosols.

horizon. The decrease in silica is attributable to two factors: an increase in the amount of clay in the A horizon, and desilication due to destruction of silicates. The increase in Fe_2O_3 toward the top of the paleosol is probably the result of oxidization of iron on exposure to atmospheric oxygen. The iron is now mostly present within hematite, but originally may have been within a variety of oxides or oxyhydrates (Walker, 1967). The Potters Mills clay also shows an increase in alumina in its A horizon, which corresponds to the increase in clay toward the top of the paleosol. The Faust Flat silty clay does not show so clearly the pedogenic trends evident in the Potters Mills clay. There is a slight increase in Al_2O_3 toward the A horizon of the Faust Flat silty clay, which is largely due to originally deposited clays. The variation in these three oxides is compatible with the field evidence that the Potters Mills clay is a more strongly developed paleosol than is the Faust Flat silty clay.

Alkaline earths. The sandy layer between the paleosols has a striking increase in alkaline earth oxides (Fig. 6). In this sample, these oxides are in equimolar proportions (Fig. 8) in support of petrographic observations that this rock is cemented by dolomite, which was also found to be the main carbonate mineral of the Juniata Formation by Horowitz (1965). Dolomitic nodules and cement correspond in abundance to the complementary variation in MgO and CaO through the entire profile, although the molar excess of MgO outside the intervening sandy layer (Fig. 8) means that much MgO is within chlorite, as noted for these rocks by Horowitz (1965) and Thompson (1970b). Of the two paleosols, the Potters Mills clay shows the most significant variations in these oxides. About 15 cm below the surface of the Potters Mills clay there is an increase in CaO of approximately 0.03 gm/cc, and the MgO content of the paleosol is 0.08 gm/cc. This finding has been interpreted as the depth to the calcic horizon. The Faust Flat silty clay, which is devoid of caliche nodules, has low values

of both oxides (<0.02 for CaO and <0.075 for MgO) throughout.

Alkalis. Of the alkali elements, there is a surficial depletion of soda in the Potters Mills clay, but an enrichment of potash (Fig. 6). This surficial accumulation is anomalous because the other bases (MgO, CaO, and Na_2) have all been leached from the upper portions of the Potters Mills clay. In modern soils, potassium enrichment may be the result of dry evaporitic conditions that cause accumulation of alkalis in the soil (Duchafour, 1982). As no corresponding enrichment in sodium is seen, this is an unlikely explanation. Potassium enrichments have been documented in many early Paleozoic and Precambrian paleosols (Gay and Grandstaff, 1980; Retallack, 1986a). Why potassium enrichment is so widespread in paleosols of early Paleozoic age and older has sparked some controversy. Studies on modern vegetation have shown that vascular plants have a remarkable ability to extract potassium from soil (Mehlich and Drake, 1955). Thus it is possible that, prior to the development of vascular plants, potassium was not removed from the soil in such great quantities (Weaver, 1967).

Another explanation for the K_2O enrichment is that it is a diagenetic phenomenon. Illitization of clays with depth has been documented in several studies (Hower and others, 1976). Morton (1985) has studied diagenetic illitization in Oligocene shales. His isotopic data indicate that the illitization of smectite has been punctuated. At depths of about 2 to 3 km, smectites were converted to illite with potassium liberated from the dissolution of potassium feldspar. This process was terminated by a local de-watering event. The degree to which potash enrichment is original or late diagenetic must be considered on a case-by-case basis.

The linear relationship between moles of K_2O and Al_2O_3 in the Juniata paleosols (Fig. 9) is an indication that the amount of potash is close to monominerally controlled. The composition

of illite usually varies between $K_2Al_4(Si_6Al_2O_{20})(OH)_4$ and $K_{1.5}Al_4(Si_{6.5}Al_{1.5}O_{20})(OH)_4$ (Deer and others, 1966), with 5:1 to 11:3 ratios of aluminum to potassium. The composition of the paleosols from the Juniata Formation is at or above this usual range, and approaches the molar proportions found in sericite and muscovite (Figs. 8, 9). All three minerals appear to be present. The main clay mineral revealed by X-ray diffraction studies is illite (Horowitz, 1965; Thompson, 1970b). Some of the recrystallized clay in the surface horizon of the Potters Mills clay could be sericite. Muscovite is rare toward the base of both paleosols. Within sandy lower horizons of the paleosols, K-feldspar also is more common. Dissolution of some of these grains could have contributed to illitization and sericitization of whatever clay minerals were once present at the surface of the Potters Mills clay. On the other hand, the Al_2O_3/K_2O ratios of the Faust Flat silty clay and the base of the Potters Mills clay are compatible with the presence of less weathered muscovite and K-feldspar there. The upper part of the Faust Flat silty clay and the sandy bed between the paleosols are now stoichiometrically illitic, and there are other reasons for supposing that some illite was originally present. The degree of weathering of the Potters Mills clay is mild by comparison with modern tropical kaolinitic soils, and there are no soil structures present which could be interpreted as evidence of large amounts of strongly swelling clays (smectites). Thus it is likely that both illite and potash were present in more than trace amounts throughout this soil, although it is difficult to be certain whether they were sufficiently abundant so that, like clay in this profile, they also increased in amount toward the surface. Some of this surficial clay may originally have been smectitic, mixed layer, or other kinds of clay.

Trace elements. Each trace element within these sedimentary rocks is present in amounts (Table 1) compatible with their derivation from a source terrain of sedimentary and metamorphic rocks of granitic to intermediate overall composition, as also determined by Krynine (1940) and Krynine and Tuttle (1941), from examination of heavy minerals. The enrichment of almost all the trace elements (excepting Co) toward the base of the Potters Mills clay paleosol (Fig. 7) can be related to the greater abundance of unweathered heavy and mafic minerals there. The distribution of Zr most clearly illustrates an original concentration of heavy minerals toward the base of the fining-upward sequence of sediment on which the paleosol formed. This element is present primarily in the extremely weather-resistant mineral zircon, which in these rocks is quite coarse-grained (Krynine, 1940). Zirconium also is much less abundant toward the top of the Faust Flat silty clay paleosol, probably for much the same reason. All other trace elements within the Faust Flat paleosol show different and much less variation than in the Potters Mills paleosol, thus confirming its lesser degree of development on a different sedimentary unit.

Apart from these patterns reflecting original sedimentation, there are two pedogenic patterns of trace elements in the Potters Mills clay paleosol: greater abundance at the surface (in Ba, Cr, Sc, V, Zn) and lesser abundance at the surface (Co, Li, Ni, Nb,

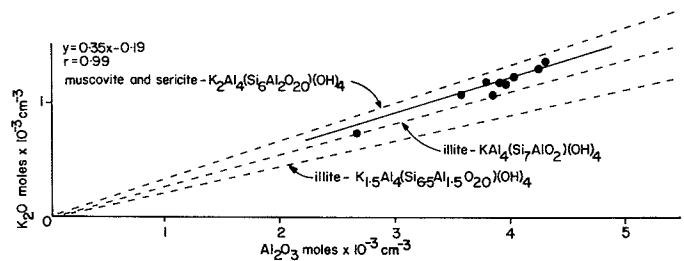


Figure 9. Molar proportions of K_2O and Al_2O_3 for both Potters Mills clay and Faust Flat silty clay paleosols (indicated by points and regression line); they fall between the usual stoichiometries for illite and sericite.

Sr, Y). There is so little Cu that not much should be made of its distribution. The upward-increasing pattern is also seen in Ti. If these data were all normalized to Ti, as is sometimes done for aridland soils when their parent material is known, those elements that appear to be surficially enriched would be seen to have remained more or less steady in abundance. Like Ti, each of these trace elements (Ba, Cr, Sc, V, and Zn) tends to accumulate in clays of soils and others residual materials (Aubert and Pinta, 1977; Wedepohl, 1978). Their distribution in the Potters Mills clay can be related to the greater abundance of clay at its surface (Fig. 5). Surficial weathering of the original sediment, together with later fine-grained additions of windblown dust and flood-borne clay, presumably enriched these weather-resistant elements.

Of the trace elements that are depleted at the surface, only Co shows a pattern completely consistent with its incorporation within carbonate (compare Fig. 5). The other surficially depleted trace elements (Li, Nb, Ni, Sr, and Y), like P, appear to have been depleted from the surface of the paleosol by destruction of rock fragments and weatherable minerals during soil formation. There is no suggestion in this paleosol of surficial enrichment of P, Ni, or Y often associated with the accumulation of well-humified organic matter within modern soils. Zinc usually follows these elements in modern soils (Kovda and others, 1964; Aubert and Pinta, 1977) and is more abundant at the surface of the paleosol, but its pattern can be related to the distribution of clay in the paleosol. Thus, the distribution of phosphorus and organic matter in the original soil was probably unlike that of modern grassland and swampy soils, and more like tropical or forested soils. In these, most of the organic matter is loose litter and living organisms, rather than incorporated within the soil (Stevenson, 1969; Smeck, 1973). As another alternative, it could be that most of the biomass of the soil was well below the surface, sheltered from a harsh external environment. Considering the profound weathering of the uppermost sample, we believe the hypothesis of subterranean communities is less likely than that of a surficial carpet of loose vegetation and litter.

Molecular ratios

Molecular ratios provide a simple index for weathering in paleosols. The ratios are determined by dividing the weight percent of each oxide involved by its molecular weight, and then dividing the oxides as specified by the particular ratio. These ratios are expressed as a single value, thereby easily allowing comparisons to be drawn between various profiles. Different ratios of oxides have been developed to assess desilication, ferruginization, leaching, waterlogging, and other effects of weathering from one horizon to the next. We also calculated two additional molecular ratios (MgO/CaO and Al_2O_3/K_2O) in order to investigate the mineralogy of carbonate and clay within the profile, as already discussed.

The ratios of $Fe_2O_3:FeO$, $SiO_2:Al_2O_3$, and $SiO_2:Fe_2O_3$ exhibit typical pedogenic trends (Fig. 8) that are indicative of ferruginization and desilication in the Juniata paleosols. The bounding unconformities that separate the individual sedimentary units on which paleosols formed are represented in our figures by undulating connecting lines. Two paleosols—Potters Mills clay and Faust Flat silty clay—are present in this profile. The intervening horizon is a sandy depositional unit that shows no soil development and is compositionally distinct from the two paleosols.

The $Fe_2O_3:FeO$ ratio shows a strong increase in oxidized iron toward the top of the Potters Mills clay paleosol. This ferruginization is marked in the Potters Mills clay, compared to the Faust Flat silty clay, which shows virtually no change in $Fe_2O_3:FeO$ with depth. The intervening sandy bed has a $Fe_2O_3:FeO$ ratio similar to the Faust Flat silty clay and the C horizon of the Potters Mills clay.

The $SiO_2:Al_2O_3$ values reflect clay content. A typical sodic feldspar, $NaAlSi_3O_8$, has a 3:1 ratio of silica to aluminum, whereas clays such as illite, $KAl_4(Si_7AlO_{20})(OH)_4$, have a 7:5 ratio. A decreasing ratio of silica to alumina indicates an increased proportion of clay minerals produced by either original sedimentation or by hydrolysis of the original silicates. Both the Potters Mills clay and the Faust Flat silty clay were developed within similar fining-upward cycles, but the Potters Mills clay has markedly increased Al_2O_3 relative to SiO_2 at the top of the paleosol. No such trend is evident in the Faust Flat silty clay. We interpret this difference in compositional variation to be largely the result of pedogenic clay formation. This is to be expected, since the Potters Mills clay is the better developed of the two paleosols. The intervening sandy layer has an extremely high ratio of $SiO_2:Al_2O_3$, reflecting its quartz-rich composition.

As with the other ratios, the Faust Flat silty clay exhibits little variation in $SiO_2:Fe_2O_3$ with depth. The uppermost portion of the Potters Mills clay, on the other hand, is depleted in SiO_2 relative to Fe_2O_3 , presumably because of fixation of iron by oxidation after desilication due to weathering (Birkeland, 1984). Krauskopf (1979) has shown that the solubility of quartz increases exponentially under conditions of $pH > 9$. A pH of at least 7 is indicated by the presence of caliche nodules, but no pseudomorphs or other evidence of highly alkaline evaporite

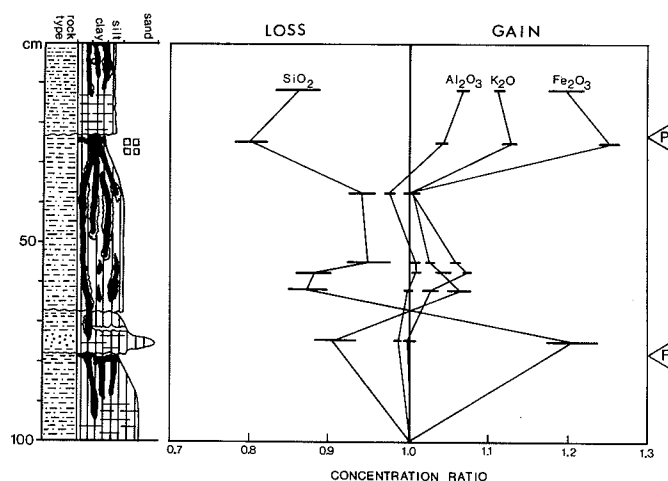


Figure 10. Concentration ratios showing gains and losses of major oxides relative to TiO_2 in Potters Mills clay (below upper triangle) and Faust Flat silty clay (below lower triangle) paleosols.

minerals have been seen. The depletion of silica from the A horizon of the Potters Mills clay is more likely due to destruction of other silicate minerals during weathering. Both rock fragments and micas become very scarce toward the top of the Potters Mills clay.

Since strontium is more soluble than the otherwise chemically similar barium, the ratio Ba/Sr is an indicator of leaching. This ratio increases with degree of drainage and with intensity and time of weathering, from near 2 in most rocks to 10 or more in strongly leached sandy soils such as Spodosols (Vinogradov, 1959). These ratios for paleosols of the Juniata Formation confirm that the Potters Mills clay, especially its surface, was much better drained and weathered longer than the Faust Flat silty clay.

Concentration ratios

To better assess the nature and degree of pedogenesis, concentration ratios were calculated for the major oxides (Fig. 10). For these calculations we have assumed that TiO_2 was stable throughout the profile. Minerals containing TiO_2 are virtually insoluble when soil conditions are moderately alkaline (Birkeland, 1984). Within the Juniata paleosols, alkaline conditions are indicated by the presence of caliche nodules. Conservation of TiO_2 is further supported by the virtually constant values of TiO_2 throughout the profile (Table 1). To establish actual concentrations or depletions, it is also necessary to know the original composition. Characterizing parent material has often been a problem for soil chemists (Krauskopf, 1979; Birkeland, 1984). Unaltered, uniform parent material is seldom encountered. This is especially a problem in fluvial sediments that include original sedimentary layering and fining-upward sequences. No single homogeneous

parent material is available for the Potters Mills clay paleosol. In light of this, a different approach for approximating a reasonable parent material composition was employed.

Field examination and the chemical variation both provide evidence that the Faust Flat silty clay is much less pedogenically developed than the Potters Mills clay. Yet both developed on similar alluvial deposits. Based on this genetic similarity, the sandy through clayey horizons of the Faust Flat silty clay may be taken to approximate the compositional range of the parent materials for the Potters Mills clay. Thus the concentration ratios calculated for the Potters Mills clay represents the result of soil formation beyond that seen in the Faust Flat silty clay. A range of concentration ratios is gained, depending on whether clayey or sandy parts of the Faust Flat silty clay were used in the calculations as a parent material. This range can be envisaged as a kind of systematic error (represented by the heavily ruled horizontal bars in Fig. 10). The concentration ratio values for the individual oxides were calculated using the following equation (after Gay and Grandstaff, 1980):

$$CR = (M_w/M_p)/(TiO_{2w}/TiO_{2p}),$$

assuming TiO_2 is stable and, where CR = concentration ratio, M_w = concentration of the oxide in paleosol, M_p = concentration of the oxide in the parent material, TiO_{2w} = TiO_2 in paleosol, and TiO_{2p} = TiO_2 in parent material.

The concentration ratios demonstrate significant soil development of the Potters Mills clay beyond the compositional range of the Faust Flat silty clay. This is encouraging confirmation of surficial desilication, clay formation, and destruction of weatherable silicates such as mica and rock fragments, of subsurface calcification, and of ferruginization, already discussed. This degree of soil formation is slight by modern standards, but nevertheless significant.

DISCUSSION

As might be surmised, these Late Ordovician paleosols do not fit comfortably into modern soil classification schemes. The Juniata paleosols can be compared to modern grassland soils of regions with mild topographic relief and subhumid to semiarid climates. Some grassland soils have a mild degree of plant-soil interaction, somewhat similar to Late Ordovician soil formation. The presumed high degree of base saturation of the Juniata paleosols is also typical of grassland soils. Closer examination of this analogy reveals discrepancies. True grassland soils, Mollisols, have a distinct mollic epipedon (surface horizon) consisting of granular peds and masses of fine root traces. No evidence of such structures was seen in the Juniata paleosols. Also, the Juniata paleosols lack the thickness and degree of humification usually associated with Mollisols.

The red color and weak textural differentiation of the Juniata paleosols more closely allies them with Oxisols, which form in tropical to subtropical climates. These soils, however, are al-

most completely leached of cations and are generally much thicker and have a microstructure distinct from that of the Potters Mills clay or the Faust Flat silty clay paleosols. The red color of the paleosols could be in large part due to diagenetic dehydration of brown and yellow minerals.

The mild degree of weathering in the Juniata paleosols requires that they be classified as USDA Inceptisols (Potters Mills clay) and Entisols (Faust Flat silty clay). Entisols and Inceptisols are generally considered to form under short periods of weathering. Unfortunately, we have little knowledge of early Paleozoic weathering rates. Thus, it may be misleading to assume that the Potters Mills clay and Faust Flat silty clay formed in the same amount of time as a comparable modern Inceptisol or Entisol.

We can place the following constraints on Ordovician weathering regimes in alluvial settings. Surficial desilication, calcification, clay formation, and ferruginization, common to modern subtropical conditions, were effective processes in early Paleozoic soils. Despite the lack of vascular plants, large (1–21 mm diameter) animals were available to promote soil formation (by aeration and bioturbation, among other processes) by Late Ordovician time. Potassium enrichments, so widespread in other early Paleozoic and Precambrian paleosols, are also present in paleosols formed on alluvial parent materials. Both pedogenic and late diagenetic contributions to potash content seem likely, but the relative importance of these different processes remains difficult to disentangle.

CONCLUSIONS

We have identified and interpreted two Late Ordovician paleosols developed on alluvium. The weakly developed Potter Mills clay is distinguished from the very weakly developed Faust Flat silty clay by several processes: (1) the development of soil structure, soil horizons, and obliteration of bedding; (2) the presence of a caliche (Bk) horizon; (3) the degree of desilication, ferruginization, and leaching of base cations; and (4) the development of potash enrichment in the A horizon.

Three separate reductions of the chemical data were employed to assess the nature and degree of soil formation. Initial assessments of desilication, ferruginization, and other effects of weathering were provided by molecular ratios. Chemical variation diagrams illustrate the variation of the major oxides. A concentration ratio diagram was constructed on the assumption that TiO_2 was immobile during weathering. Since no homogeneous parent material was available, the range in composition of the very weakly developed Faust Flat silty clay paleosol was used to approximate a parent material composition for the Potters Mills clay paleosol. The concentration ratios show significant soil development in the Potters Mills clay beyond any soil formation in the Faust Flat silty clay. The degree of soil development is slight by modern standards, making these soils most similar to modern USDA Inceptisols and Entisols.

From our observation of the Juniata Formation at several localities in Pennsylvania, the Potters Mills clay and Faust Flat

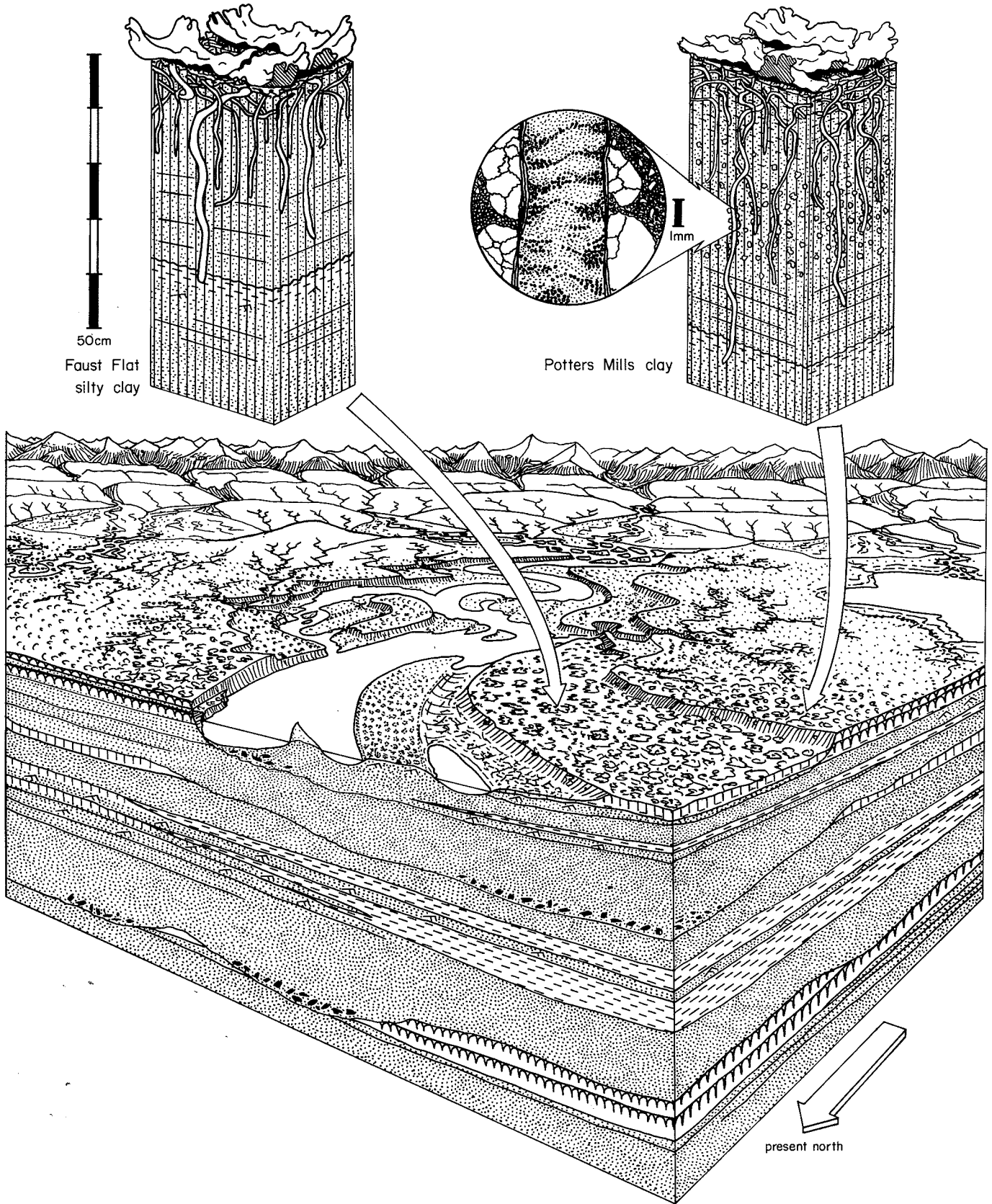


Figure 11. Late Ordovician paleoenvironmental reconstruction showing flood-plain settings for Potters Mills clay and Faust Flat silty clay paleosols. Our fluvial reconstruction is based on measurements of asymmetric paleochannels in the roadcut southeast of Potters Mills. The nature of vegetation remains unknown; maximum conceivable biomass compatible with chemical and structural features of the paleosols is shown. Nature of animals that excavated burrows with w-shaped backfill layers (shown in enlargement) is also under further investigation.

silty clay are representative of two widespread kinds of paleosols formed on inland portions of coastal plains flanking the ancestral Appalachian Mountains (Fig. 11). We envisage these soils forming on streambanks (Faust Flat Series) and low terraces (Potters Mills Series) in a landscape that would have appeared barren, yet not quite desertlike. The exact nature of vegetation in this landscape is not known. It was probably nonvascular, and much more low-growing and monotonous than modern vegetation of comparable seasonally dry subtropical climates. Traces of a low-

diversity fauna, presumably arthropods as large as 2 cm across, appear to have been considerably more uniform between the limited range of ecosystems preserved (represented by the two paleosol series) than is the case in modern subtropical landscapes. The chemical studies reported here strengthen our impression of the Juniata Formation as an important record of an early stage in the evolution of multicellular soil fauna and flora and of soil-forming processes.

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