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Soil development on moraines of Mendenhall Glacier, southeast Alaska. 2. Chemical transformations and soil micromorphology

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Abstract

Soils on Holocene-age moraines of the Mendenhall Glacier in southeast Alaska range from morphologically undeveloped to soils having field-identified spodic horizons that are more strongly expressed with increasing soil age. A soil chronosequence was sampled to study development of spodic features and to compare the expression of these features with chemical and micromorphological properties. Organic C accumulates rapidly in these soils, with O horizons forming within 38 yr. Organic C is highly correlated with cation exchange capacity ($R^2 = 0.92$), variable charge ($R^2 = 0.94$), extractable acidity ($R^2 = 0.83$), and 1500-kPa water retention ($R^2 = 0.97$). The pH of the 10-yr old pedon is acidic with a soil pH (H_2O) ranging from 5.0 to 6.4. The pH decreases with soil age, with the lowest pH in horizons at the organic/mineral contact. Increases in dithionite–citrate, sodium pyrophosphate, and acid–oxalate extractable Fe (Fe_o) are most evident in the > 240-yr old soil. Depth trends for these measured properties within pedons are most distinctive for Fe_o which increases from surface mineral horizons (A or E) to underlying horizons in all pedons. The Fe_o/Fe_d ratio increases with soil age in B horizons, and in pedons ≥ 70 yr, this ratio ranges from 0.3 to 0.5 in the E horizons and from 0.4 to 0.83 in B horizons immediately below. These data indicate a greater proportion of poorly crystalline Fe in illuvial horizons with increasing soil age. Allophane content is low (≤ 6 g kg^{-1}) in these pedons, and there is no consistent increase with soil age. The optical density of acid–oxalate extract (ODOE) and $Al_o + 1/2\ Fe_o$ are sensitive and consistent chemical indicators of spodic development. The ODOE increases with soil age in B horizons (0.06 to 0.56). The $Al_o + 1/2\ Fe_o$ also increases with soil age in B horizons (1.2 to 4.5 g kg^{-1}) and within pedons from E to B horizons. Nonoccluded Ca-bound P (195 to 49 mg kg^{-1}) and total P (700 to 300 mg kg^{-1}) decrease in E

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horizons relative to underlying horizons with soil age. Surface horizons of the younger pedons are predominantly aggregates of uncoated sand-sized grains with few organic constituents. Early processes of eluviation are evidenced by the etching of mineral grains in the E horizon of the 70-yr old pedon. There is no optical evidence of Fe-oxide accumulation in these soils, with the exception of the BC horizon of the > 240-yr old pedon. This chronosequence study indicates that spodic development is achieved within a relatively short period of time in soils of this region.

1. Introduction

Rapid mineral weathering accompanied by high rates of organic matter accumulation are common in cool, humid climates. These conditions promote the formation of E/Bs horizonation and spodic materials in a relatively short period of time (Alexander et al., 1993; Shoji et al., 1988; McDaniel et al., 1993). Soil chemical processes that form spodic materials and Spodosols have been linked to the presence of organic compounds and the translocation of Fe and Al in the form of fulvate–metal complexes (De Coninck, 1980; McKeague et al., 1983; Dahlgren and Ugolini, 1991). In situ H_3CO_3 mineral weathering (Dahlgren and Ugolini, 1991; Shoji and Yamada, 1991) and translocation of inorganic, sesquioxide and proto-imogolite sols (Farmer et al., 1980; Anderson et al., 1982; Farmer, 1982; Freeland and Evans, 1993) also may play a role in Bs horizon formation. Soil pH and solution levels of Fe, Al, or Si are additional factors in the formation of weathering products (e.g., humic/metal complexes or imogolite and allophane), their mobility, and relative contribution to the segregation and formation of spodic materials.

Soils on recessional moraines of the Mendenhall glacier have morphologically-identified E and Bs horizons forming within 70 years, and spodic horizons forming within 240 years (Alexander and Burt, 1996). Progressive development of spodic characteristics on these soils which form a chronosequence present the opportunity to study changes in chemical properties in early stages of Spodosol formation on nontephra-derived parent materials. These changes may provide information concerning active chemical processes occurring in these soils which has led to the development of spodic characteristics. The objectives of this study were to (i) determine changes in soil chemical properties as a function of soil age in a young chronosequence on the moraines of the Mendenhall Glacier; and (ii) examine micromorphologic indicators of spodic horizon development in these soils.

2. Materials and methods

Site dating techniques, vegetative succession, landforms, field macromorphology, and soil mineralogy have been described (Alexander and Burt, 1996). Sampling and laboratory analytical procedures are described in the Soil Survey Investigations Report (SSIR) No. 42 (Soil Survey Laboratory Staff, 1992). Alphanumeric codes in parentheses following each method description represent specific procedures documented in the SSIR No. 42.

In the laboratory, bulk samples were air-dried and sieved to remove rock fragments (> 2 mm). Particle-size analysis was by pipet and sieving (3A1). Saran-dipped clods were used to determine oven-dry (4A1b) and 33-kPa (4A1d) bulk density and water retention (4B1c). Water retention at 1500 kPa was determined on < 2-mm air-dried soil (4B2a).

Organic C (6A1c) was determined by acid–dichromate digestion and $FeSO_4$ titration. Cation exchange capacity (CEC) was determined with NH_4OAc buffered at pH 7.0 (CEC-7) (5A8b). The CEC by sum of cations (5A3a) was determined by summing the NH_4OAc-extractable bases (5B5a) plus the acidity extracted with $BaCl_2$–TEA, pH 8.2 (6H5a). The variable charge is the numerical difference between CEC by sum of cations and CEC-7. Soil pH (H_2O) was determined in a 1 : 1 soil water paste (8C1f). Exchangeable Al was extracted with 1 M KCl and determined by inductively coupled spectrometry (6G9b). Aluminum saturation was calculated by dividing KCl-extractable Al by the sum of the NH_4OAc-extractable bases plus KCl-extractable Al and multiplying by 100 (5G1). Dithionite–citrate (6C2b, 6G7a, 6D2a), sodium pyrophosphate (6C8a, 6G10a), and acid oxalate (6C6a, 6V2a, 6G12a) extracts were analyzed for Fe, Al, and Si, respectively. The optical density of the acid oxalate extract (8J) was also determined. Allophane contents were calculated by the method of Parfitt (Parfitt and Henmi, 1982; Parfitt and Wilson, 1985). NaF pH was determined in 1 M NaF (8C1d). New Zealand P retention was determined using a 1000-ppm P solution (6S4). The sequential fractionation of soil P (Chang and Jackson, 1957; Olsen and Sommers, 1982) included three discrete classes of compounds (Al, Fe, and Ca phosphates) including possible occluded P within coatings of Fe oxides and hydrated oxides. Extractable P was determined by Bray P-1 procedure (6S3). Total Fe and P were obtained by hydrofluoric (HF) acid digestion (7C3) on the < 2-mm fraction. Total N was determined by the Kjeldahl technique (6R3).

Thin sections were produced by resin impregnation of natural fabric samples (4E1). Samples of natural fabric were mounted on Al stubs, sputter coated with gold in a vacuum separator, and examined with a scanning electron microscope (SEM) operating at 20 kV. Information from SEM is based on fabric and grain morphology, and laboratory data.

3. Results and discussion

3.1. Chemical properties

Properties of the youngest pedon (10 yr) (Table 1) serve as a baseline for soil development on the moraines of the Mendenhall Glacier. Low and relatively uniform organic C (0.2 to 0.4 g kg^{-1}), CEC (2.0 to 2.1 cmol kg^{-1}), and extractable bases (2.0 to 2.3 cmol kg^{-1}) are present with depth. The pH (H_2O) is acidic, ranging from 5.0 at the surface to 6.4 in the lowest horizon.

Organic horizons form and differentiate within 38 yr (Table 1; Alexander and Burt, 1996). Organic C is increasingly redistributed to greater depths with soil age (Table 1). Initially, organic C accumulation (kg m^{-2}) in the upper mineral horizons is low due to

Table 1
Chemical properties on < 2-mm air-dried fraction of sampled pedons

Horizon	Depth (cm)	Organic C (g/kg)	1500 kPa H_2O (%)	pH (H_2O)	Acidity $BaCl_2$–TEA (cmol/kg)	CEC pH 7 (cmol/kg)	Bases pH 7 (cmol/kg)	Al KCl extr. (cmol/kg)	Al sat. (%)	C/N
Pedon 1 (10 yr)										
A1	0–5	0.4	0.4	5.0	17.1	2.1	2.3	TR [a]	nd [b]	nd
C1	5–22	0.3	0.3	5.1	9.0	2.0	2.1	TR	nd	nd
C2	22–100	0.2	0.2	6.4	3.2	2.1	2.0	nd	nd	nd
Pedon 2 (38 yr)										
Oi	5–4	425	50.7	6.0	36.8	79.7	77.6	nd	nd	nd
Oe	4–0	197	26.5	5.8	23.5	44.2	37.3	nd	nd	nd
A	0–12	2.3	1.1	5.3	1.6	2.0	1.3	0.2	13	nd
C1	12–48	0.8	1.3	5.9	0.8	1.7	1.5	nd	nd	nd
C2	48–100	0.5	0.8	6.2	0.9	1.4	1.7	nd	nd	nd
Pedon 3 (70 yr)										
Oi	10–9	534	69.3	5.5	57.0	101.5	79.4	nd	nd	nd
Oe	9–5	406	56.3	4.9	61.7	78.2	42.7	0.2	TR	nd
Oa	5–0	275	35.8	5.5	53.9	62.7	28.5	0.4	1	nd
E	0–4	18.8	4.0	5.0	4.3	5.7	3.0	0.2	6	16
Bs	4–10	3.9	1.1	4.6	2.5	2.0	1.0	0.4	29	16
C1	18–56	2.1	1.0	5.1	1.5	1.5	0.8	0.3	27	nd
C2	56–90	1.8	1.1	5.3	1.3	1.6	0.9	0.3	25	nd
Pedon 4 (90 yr)										
Oi	10–8	591	61.6	5.9	52.1	71.6	58.7	2.8	5	nd
Oe	8–4	595	62.3	4.2	90.7	92.4	37.4	0.3	1	nd
Oa	4–0	492	62.4	3.8	112.3	107.4	38.3	1.1	3	nd
E	0–3	21.8	5.2	4.6	7.9	7.4	1.9	1.5	44	26
Bs	3–9	6.1	1.8	5.2	3.8	2.9	1.1	0.6	35	24
C1	9–42	2.4	1.8	5.4	2.4	1.9	1.2	0.3	20	nd
C2	42–100	0.7	0.6	5.6	0.5	0.9	1.0	TR	nd	nd

Pedon 5 (240 yr)										
Oi	7–4	536	58.0	5.2	77.7	75.8	36.9	0.4	1	nd
Oe	4–2	533	76.3	3.9	115.9	105.9	28.6	1.9	6	nd
Oa	2–0	533	64.0	3.7	116.6	106.2	24.4	1.8	7	nd
E	0–4	60.6	13.7	4.3	17.4	14.1	3.1	1.7	35	33
Bhs	4–14	16.6	3.3	4.8	9.1	7.0	1.0	1.6	62	35
BC	14–21	4.4	1.4	5.0	3.3	2.5	0.9	0.4	31	34
C1	21–33	3.9	1.2	5.2	2.8	2.4	1.0	0.4	29	24
C2	33–93	1.0	0.6	5.5	0.9	1.0	0.6	nd	nd	nd
Pedon 6 (> 240 yr)										
Oi	18–17	599	60.0	4.7	75.8	68.0	33.0	0.3	1	nd
Oe	17–10	572	59.1	4.2	99.6	83.8	23.4	1.1	4	nd
Oa	10–0	433	47.6	3.4	117.6	100.2	22.4	1.9	8	nd
E	0–2	24.6	6.9	4.7	8.7	7.9	1.7	1.0	37	30
Bh	2–9	39.9	8.9	4.4	23.5	18.6	2.4	4.3	64	24
BC	9–24	20.6	5.4	4.8	14.0	10.0	1.8	2.1	54	30
2C	24–42	21.8	5.0	4.9	14.2	11.0	2.3	2.1	48	32

[a] Tr = trace.
[b] nd = not determined.

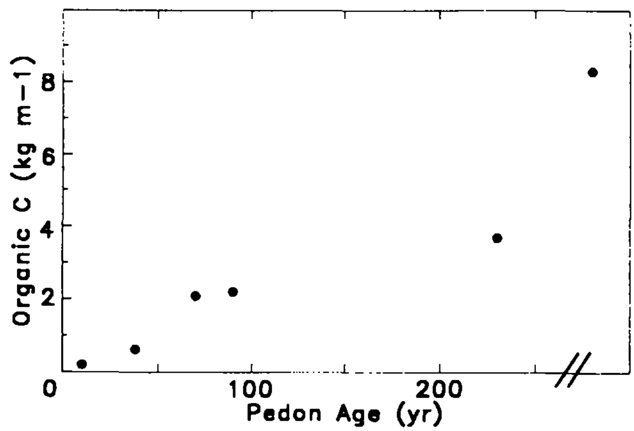


Fig. 1. Organic carbon accumulation for upper 40 cm of mineral soil of sampled pedons. Bulk density at 33-kPa water retention (measured or predicted) and volume percent of rock fragments (Table 4 in Alexander and Burt, 1996) are used in this conversion.

slight vegetative cover but increases significantly as the forest becomes established (Fig. 1). In all pedons except the oldest soil (> 240 yr), organic C accumulates in surface mineral horizons (A or E) and decreases sharply with depth. In the > 240-yr old pedon, organic C is more uniform with depth, with a maximum mineral horizon humus accumulation in the Bh horizon.

Organic C is an important factor in the development of these soils as evidenced by the changes in chemical properties with soil age. In the 38-yr old pedon, CEC is relatively high in the Oi and Oe horizons (79.7 and 44.2 cmol kg^{-1}, respectively) but low in mineral horizons (2.0 to 1.4 cmol kg^{-1}). The low CEC is comparable to the CEC in the 10-yr old pedon and is related to the low organic C (≤ 2.3 g kg^{-1}) in these horizons. As organic C increases in surface and subsurface mineral horizons with soil age, the CEC increases accordingly. The CEC of the 2C horizon of the oldest pedon (> 240 yr) is 11.0 cmol kg^{-1}, reflecting the relatively high organic C (21.8 g kg^{-1}) in the subsoil of this pedon compared to subsoil horizons of younger pedons. Overall, the CEC in all horizons (mineral and organic) is positively correlated ($n = 37$) with increasing organic C ($R^2 = 0.92$). Other soil properties (Table 2) are also positively correlated with organic C (Fig. 2), e.g., variable charge ($R^2 = 0.94$), extractable acidity ($R^2 = 0.83$), and 1500-kPa water retention ($R^2 = 0.97$).

The average pH (H_2O) for soil mineral horizons increases from 5.5 in the 10-yr old pedon to 5.8 in the 38-yr old pedon, but decreases to 5.0–5.2 in the 70 to 240 yr old pedons, and finally decreases to 4.7 in the oldest pedon (> 240 yr). The lowest mineral horizon in these soils exhibits a continual decrease in pH (H_2O) with soil age from 6.4 in the youngest (10 yr) to 4.9 in the oldest (> 240 yr) pedon. The most acidic horizons within pedons are those at the organic/mineral contact. In pedons ≥ 70 yr old, the Oa and E horizons generally have a lower pH (H_2O) relative to other horizons within pedons, with the lowest pH in Oa horizons. This trend suggests that acidity is generated from organic matter mineralization and that this acidity is translocated into surface

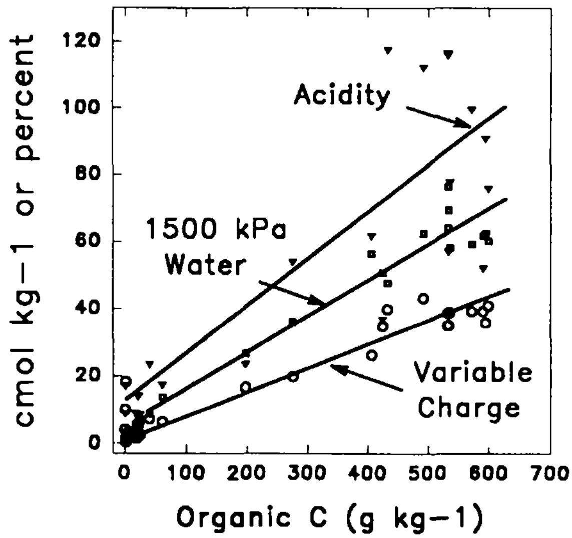


Fig. 2. Relationship between organic C and three properties for organic and mineral horizons of sampled pedons: extractable acidity (triangles, expressed as cmol kg^{-1}); 1500-kPa water retention (squares, percent); and variable charge (circles, cmol kg^{-1}). Lines represent the linear regression of these data with organic C. R^2 is 0.83, 0.97, and 0.94 for acidity, water retention, and variable charge, respectively.

mineral horizons and likely below. Soluble organic acids dissolved from plant residues are important agents in weathering reactions in Spodosols (Ugolini et al., 1988, 1991). This process results in a general decrease in soil pH (H_2O) for these soils.

Extractable bases are low and relatively uniform ($\approx$ 2.1 cmol kg^{-1}) with depth in the youngest pedon (10 yr). With establishment of vegetation and development of O horizons in the 38-yr old pedon, relatively high amounts of extractable bases (37.3 to 77.6 cmol kg^{-1}) accumulate in these horizons. This accumulation of bases in the surface of the 38-yr old pedon, as well as the slight decrease in bases ($\approx$ 1.6 cmol kg^{-1}) in the lower mineral horizons, suggest that the release of bases from minerals by organic acid weathering, followed by plant absorption and base cycling, are sufficiently established processes to create differences in chemical properties between horizons.

Extractable bases decrease to 0.9–1.0 cmol kg^{-1} in subsoil horizons of the 70-yr old pedon but remain relatively constant, decreasing only slightly from this amount in any horizon of older pedons. This trend suggests that while bases are being removed by both leaching of organic acids and plant absorption, soil minerals, e.g., biotite, plagioclase feldspar, and/or hornblende (Alexander and Burt, 1996), are weathering at a sufficient rate to produce a small, but continual supply of basic cations.

The decrease in pH (H_2O) with soil age is also reflected in an increase in extractable Al and Al saturation (Table 1). Extractable Al increases in B horizons (0.4 to 4.3 cmol kg^{-1}), and Al saturation reaches a maximum of 64 percent in the Bh horizon of the > 240-yr old pedon. Even though all pedons in this study are acidic, KCl-extractable Al values are relatively low in both organic and mineral horizons, and Al saturation is very low in organic horizons. These low amounts are indicative of the relative high cation

Table 2
Chemical dissolution data on < 2-mm air-dried fraction of mineral horizons of sampled pedons

Horizon	(g/kg)								Fe_o/Fe_d	Al/Si [c]	Allophane (g/kg)	pH NaF	P ret. (%)	Al_o + 1/2 Fe_o (g/kg)	ODOE
	Fe_d	Fe_p	Fe_o	Fe_t	Al_d	Al_p	Al_o	Si_o							
Pedon 1 (10 yr)															
A1	2	1	1.1	31	– [a]	TR [b]	0.3	0.2	0.55	nd [d]	nd	8.0	1	0.9	0.03
C1	2	TR	1.6	36	–	TR	0.2	0.2	0.80	1.0	1	7.9	13	1.0	0.05
C2	1	–	0.9	36	–	TR	0.2	0.1	0.90	nd	nd	8.0	6	0.7	0.03
Pedon 2 (38 yr)															
A	3	–	1.5	35	1	1	0.6	0.4	0.50	nd	nd	9.1	16	1.4	0.05
C1	3	1	2.0	35	1	1	0.6	0.5	0.67	nd	nd	9.0	13	1.6	0.05
C2	3	–	1.6	34	–	–	0.4	0.3	0.53	1.4	2	8.8	13	1.2	0.03
Pedon 3 (70 yr)															
E	2	TR	0.6	30	TR	–	0.3	TR	0.30	nd	nd	7.7	9	0.6	0.05
Bs	3	TR	1.2	33	1	–	0.6	0.2	0.40	3.1	1	9.2	13	1.2	0.06
C1	3	–	1.4	34	1	TR	0.7	0.3	0.47	2.4	2	9.5	9	1.4	0.06
C2	2	–	1.5	37	1	TR	0.7	0.4	0.75	1.8	3	9.5	1	1.5	0.04
Pedon 4 (90 yr)															
E	3	1	0.9	30	1	TR	0.7	0.1	0.30	nd	nd	7.7	16	1.2	0.13
Bs	3	1	1.6	32	1	1	1.2	0.5	0.53	0.4	4	9.8	40	2.0	0.09
C1	2	TR	2.1	35	1	TR	1.3	0.8	1.05	1.7	6	9.8	nd	2.4	0.06
C2	3	–	2.6	36	1	TR	0.7	0.5	0.87	1.5	4	9.1	6	2.0	0.05

Pedon 5 (240 yr)															
E	2	1	1.0	33	1	1	0.9	TR	0.50	nd	nd	7.3	9	1.4	0.24
Bhs	4	1	3.3	56	1	1	1.0	0.2	0.83	nd	nd	9.3	27	2.7	0.24
BC	3	TR	2.7	43	1	1	0.9	0.4	0.90	nd	nd	10.0	16	2.3	0.08
C1	3	1	1.5	37	1	1	0.9	0.4	0.50	nd	nd	10.0	19	1.7	0.06
C2	3	TR	2.4	34	1	1	0.7	0.5	0.80	nd	nd	9.8	9	1.9	0.06
Pedon 6 (> 240 yr)															
E	2	1	1.0	35	1	–	0.5	TR	0.50	nd	nd	7.4	13	1.0	0.13
Bh	7	5	5.0	45	2	1	2.0	0.4	0.71	2.6	3	8.1	38	4.5	0.56
BC	7	3	4.9	39	2	1	1.9	0.4	0.70	2.3	3	9.0	32	4.4	0.33
2C	8	5	6.3	43	2	1	2.3	0.5	0.79	2.7	4	9.2	34	5.5	0.35

[a] – = analysis run but none detected.
[b] TR = trace.
[c] Al/Si = Molar ratio of $(Al_o - Al_p)/Si_o$.
[d] nd = not determined.

selectivity of organic matter exchange sites (Ping et al., 1988; Thomas and Hargrove, 1984).

The C/N ratio relates to organic matter decomposition. The C/N ratios (Table 1) range from 16 to 26 in the E and B horizons of the 70 and 90-yr old pedons but increase to > 30 for the same horizons of the 240 and > 240-yr old pedons. C/N ratios are not determined for those soil horizons with extremely low N values. High C/N ratios usually suggest low organic matter decomposition levels and/or low N levels. In Spodosols, increases in C/N ratios have been associated with longer mean residence time for organic matter (Page and Guillet, 1991). This trend suggests that the rate of organic matter flux (accumulation and mineralization) has decreased in older pedons, indicating greater stability or decreased rate of change in organic matter and other associated properties in these soils relative to younger pedons.

3.2. Selective and total dissolutions: Fe, Al, and Si

Pedogenically-derived Fe in these soils, as indicated by dithionite citrate-extractable Fe (Fe_d), is low (< 10 g kg^{-1}). Increases in Fe_d, sodium pyrophosphate-extractable Fe (Fe_p), and acid oxalate-extractable Fe (Fe_o) (Table 2) are most evident in the oldest pedon (> 240-yr). Depth trends for these properties within pedons are most distinctive for Fe_o, which increases from surface mineral (A or E) horizons to underlying horizons in all pedons. The Fe_d is considered to be a measure of total pedogenic Fe, while Fe_o is a measure of poorly crystalline Fe, e.g., ferrihydrite (Birkeland et al., 1989), plus organic-bound Fe (Wada, 1989). The Fe_p has been correlated with organic-bound Fe (Parfitt and Childs, 1988; Schwertmann and Taylor, 1989). Fe_d ranges from 1 g kg^{-1} in the C2 horizon of the youngest pedon (10 yr) to a maximum of 8 g kg^{-1} in the 2C horizon of the oldest pedon (> 240 yr). Fe_o ranges from 0.9 to 6.3 g kg^{-1} in these same horizons, while Fe_p ranges from nearly zero to a maximum of 5 g kg^{-1}.

The 70-yr old pedon is the youngest soil in this chronosequence study in which a Bs horizon is identified by macromorphology. In this pedon, there is a two-fold increase in Fe_o in the subsoil compared to the surface horizon. This Fe_o increase suggests that the acidity generated in O horizons dissolves soil minerals and releases Fe which is then translocated to lower horizons. Farmer et al. (1985) supported acidic weathering of plagioclase and biotite in E horizons as a mode in Bs horizon formation. Largest differences in free Fe-oxide (Fe_d and Fe_o) between surface mineral (A or E horizons) and underlying horizons are most evident in the 240-yr old pedon with 2 and 1.0 g kg^{-1} Fe_d and Fe_o, respectively, in the E horizon and 7.0 and 5.0 g kg^{-1} Fe_d and Fe_o, respectively, in the Bh horizon.

Fe_d and Fe_o are consistently high in all lower horizons of the > 240-yr old pedon. This relatively high Fe is not likely explained by translocation processes alone. The total Fe (Fe_t) in this pedon shows no significant increase with depth, relative to the E horizon, especially when viewed in context of the younger pedons. Fe_t indicates that no extensive dissolution and translocation of Fe has occurred from upper horizons. Relatively high Fe_d and Fe_o in subsoil horizons suggest that in situ weathering of soil minerals release Fe and form both crystalline (goethite) and poorly crystalline (ferrihydrite) Fe oxides in this pedon. The fulvate–carbonate theory (Dahlgren and Ugolini,

1991) proposes that in situ weathering of minerals by H_3CO_3 occurs in lower horizons of Spodosols, accounting for secondary mineral formation in excess of those minerals which may be translocated from overlying horizons by fulvic acid released by organic matter mineralization.

The ratio of Fe_o/Fe_d has been called an "activity ratio" and has been used as a relative measure of the crystallinity of free iron oxides (Schwertmann, 1985). Similar to Fe_o, differences in the Fe_o/Fe_d within pedons are evident between the E and its underlying horizon. In pedons $\geq$ 70 yr, the Fe_o/Fe_d ranges from 0.3 to 0.5 in the E horizons and from 0.4 to 0.83 in the B horizons immediately below. This indicates that there is a greater proportion of poorly crystalline Fe (relative to total pedogenic Fe) in B horizons, suggesting that poorly crystalline Fe, such as ferrihydrite, is less stable in the E horizons. The decreased proportion of poorly crystalline Fe may be related in part to both soil pH and the greater concentration of organic acids which are likely present in the E horizons relative to the underlying horizon. Organic acids lower pH and complex Fe and Al, preventing formation of ferrihydrite.

Fe_o/Fe_d increases with soil age in B horizons, increasing from 0.40 in the Bs horizon of the 70-yr old pedon to 0.83 and 0.71 in the Bhs and Bh horizons of the 240 and > 240-yr old pedons, respectively. Higher Fe_o/Fe_d ratios indicates that a greater proportion of the free Fe in older soils exists in poorly or noncrystalline forms (Kodama and Wang, 1989). Similar trends in pedogenic Fe gradients were obtained by Singleton and Lavkulich (1987) in a chronosequence study of coastal British Columbia soils.

The Fe_p/Fe_o ratios are higher in E horizons of the 90, 240, and > 240-yr old pedons than in the underlying B horizons. Fe_p/Fe_o is 1 in E horizons, whereas these ratios are 0.6, 0.3, and 0.6 in the Bs, Bhs, and BC horizons, respectively, for these same pedons. This decrease indicates that nearly all of the active Fe in eluvial horizons is complexed with humus, whereas there is some formation of inorganic Fe minerals in underlying spodic horizons.

The Fe extractions indicate translocation from E to B horizons more clearly than do Al extractions. Al_o, Al_p, and Al_d are very low in all pedons, and $Fe_o > Al_o$ in all horizons. The Al_o increases from E to B horizons (Table 2), but depth trends within pedons for Al_d and Al_p (Table 2) are inconsistent. Acid-oxalate extractable Al (Al_o) is generally an estimate of total pedogenic Al and much of it may be in allophane, imogolite, and complexed with organic matter (Childs et al., 1983; Wada, 1989). Unlike Fe_d, the dithionite-citrate extractable Al (Al_d) is not always greater than Al_o (Birkeland et al., 1989; Childs et al., 1983) and so does not necessarily represent total pedogenic Al (Wada, 1989).

Allophane, a poorly crystalline aluminosilicate, is present in only very small amounts ($\leq$ 6 g kg^{-1}) in these pedons (Table 2), and there is no consistent increase in allophane with soil age. Allophane with a Al/Si molar ratio of 2.0 is considered a reference point in the allophane series of aluminosilicates (Parfitt and Henmi, 1982). Since the average Al/Si molar ratio of these soils (Table 2) is close to 2, the allophane was estimated by the formula $Si_o \times 7.14$ (Parfitt and Henmi, 1982; Parfitt and Wilson, 1985). The Al/Si ratios are not determined if the $Al_p \approx Al_o$ and/or the Si_o is very low. In those instances in which $Al_p \approx Al_o$, all or most of the Al is assumed to be bound in humus complexes. Those horizons in which $Al_p > Al_o$ result from the greater degree of error in determining such low amounts. The very low Si_o values are found in the leached E horizons of these pedons. Allophane is unlikely to be present in E or B horizons because soil pH < 4.8, an unfavorable environment for allophane stability (Wada, 1985).

High fluoride reactivity and P retention are associated with plentiful active Al or Al_o (Shoji and Fujiwara, 1984; Shoji et al., 1985). The NaF pH test has been used as a simple and convenient index of andic materials. As a rule of thumb, a NaF pH ≥ 9.4 is a strong indicator that andic materials (allophane) dominate the exchange complex (Fieldes and Perrott, 1966). In many ways, P retention is a duplicate of the information provided by the NaF pH test (Uehara and Ikawa, 1985) and is based on a similar ligand exchange. NaF pH (Table 2) generally decreases in surface horizons with soil age. NaF pH ranges from 8.0 in the 10 yr old pedon to 7.4 in the 240-yr old pedon. NaF pH and P retention (Table 2) are lower in all E horizons relative to underlying horizons. NaF pH is 7.3 and 7.4 in E horizons of the 240 and > 240-yr old pedons, respectively, whereas the NaF pH in the underlying B horizons is 9.3 and 8.1 for these same pedons. These trends indicate that Al is being translocated to the lower horizons. Shoji et al. (1988) found that NaF pH is characteristically low (< 9.4) in Oa and E horizons of Spodosols.

A soil horizon consisting of spodic materials, as defined in the *Keys to Soil Taxonomy* (Soil Survey Staff, 1994), normally has an optical density of acid oxalate extract (ODOE) ≥ 0.25 or an $Al_o + 1/2\ Fe_o \geq 0.5\%$, and these values are at least two times greater than the ODOE or $Al_o + 1/2\ Fe_o$ for an overlying eluvial horizon. This increase in ODOE or $Al_o + 1/2\ Fe_o$ is considered indicative of the accumulation of translocated organic materials in an illuvial horizon. These organic materials contain Al, with or without Fe.

In this study, the ODOE and $Al_o + 1/2\ Fe_o$ (expressed as g kg^{-1}) are sensitive and consistent chemical indicators of spodic development with soil age. The $Al_o + 1/2\ Fe_o$ serves as a useful index of the translocation of Fe and Al bound by both organic and inorganic constituents. The $Al_o + 1/2\ Fe_o$ increases with soil age in B horizons (1.2 to 4.5 g kg^{-1}) and within pedons from E to B horizons.

The ODOE (Table 2) increases with soil age in B horizons (0.06 to 0.56), and the depth trends from E to B horizons indicate that cumulative podzolization increases with soil age. In the 90 yr-old pedon, the ODOE is greater in the E horizon than in the underlying illuvial horizon, equal in the 240-yr old pedon, and only in the oldest pedon is there a clear increase in ODOE from an eluvial albic horizon to an illuvial Bh horizon. Acid oxalate is considered a poor extractant for humic acid (Bascomb, 1968), and the ODOE has been used as an indicator for the presence of fulvic acids (Daly, 1982; Barrett and Schaetzl, 1992), which may be an important organic matter fraction in the translocation of Fe and Al in Spodosols (De Coninck, 1980).

The ODOE distribution may not necessarily mirror the soil organic matter distribution (Barrett and Schaetzl, 1992). In the 240-yr old pedon, the organic C in the E horizon is nearly four times that in the Bhs horizon, but the ODOE is the same for both horizons (0.24).

3.3. Fractionated and total phosphorus

The leaching of calcium-bound P (Ca-P) from soil profiles is an effective indicator of relative pedogenic age in chronosequence studies (Syers and Walker, 1969; Syers et al.,

Table 3
Nonoccluded Ca-, Al- and Fe-P; total P; and available P of selected mineral horizons of sampled pedons

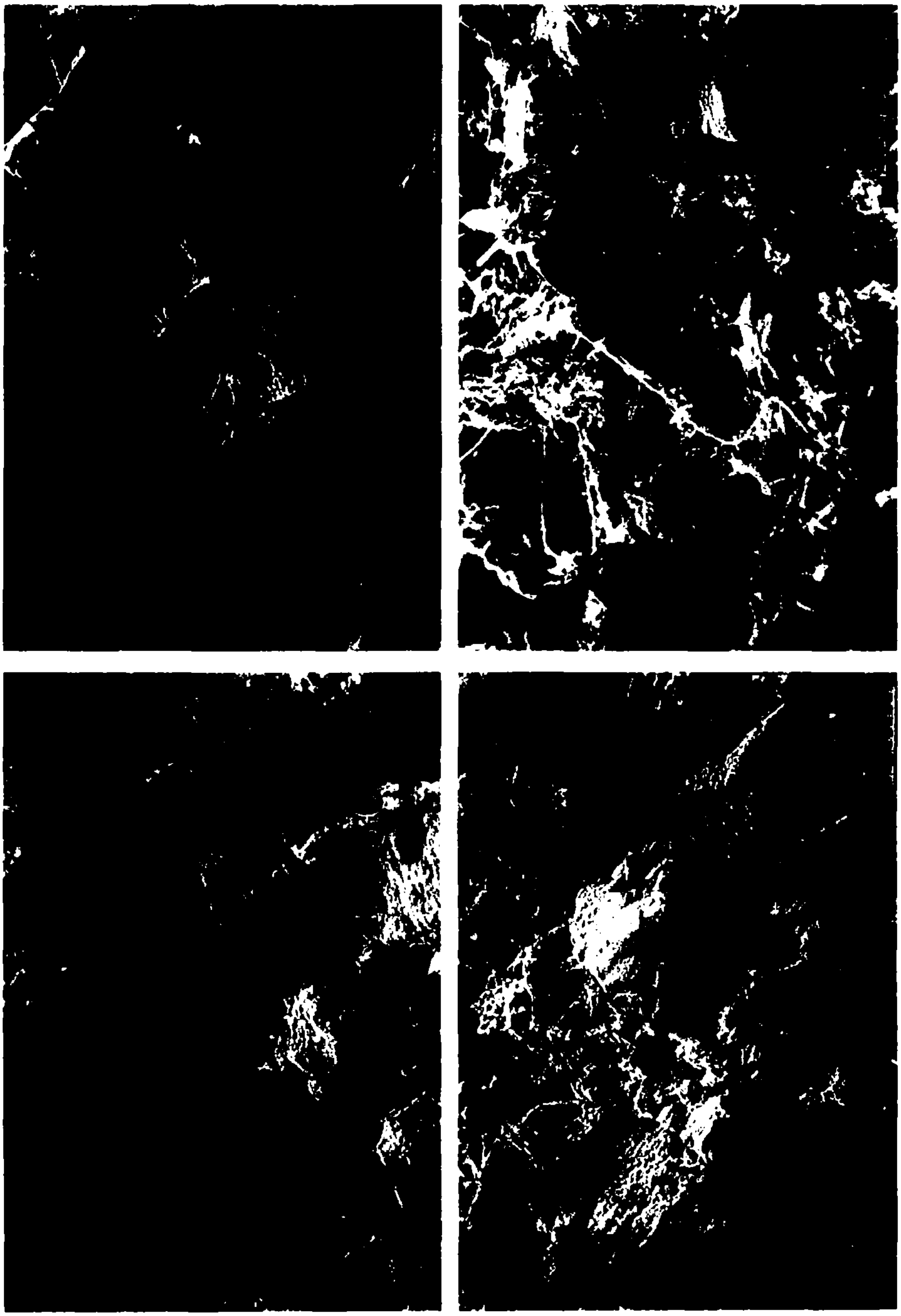
Pedon	Horizon	Ca-P (mg/kg)	Al-P + Fe-P (mg/kg)	Total P (mg/kg)	Extr. P Bray-1 (mg/kg)
Pedon 1 (10 yr)	A1	668	62	800	26
	C2	430	76	900	TR [a]
Pedon 2 (38 yr)	A	668	349	1100	2
	C2	854	215	1200	1
Pedon 3 (70 yr)	E	195	24	700	13
	Bs	699	113	1100	2
	C2	806	235	1200	4
Pedon 4 (90 yr)	E	113	71	400	25
	Bs	446	263	1000	3
	C2	668	203	900	5
Pedon 5 (240 yr)	E	104	23	400	19
	Bhs	668	24	1300	18
	BC	766	64	1300	2
	C2	699	53	1200	4
Pedon 6 (> 240 yr)	E	49	37	300	16
	Bh	269	135	400	15
	2BC	766	175	900	4
	2C	854	211	1200	1

[a] TR = trace.

1970; Adams and Walker, 1975; Walker and Syers, 1976; Singleton and Lavkulich, 1987). Total P and nonoccluded Ca-P (Table 3) decrease in E horizons with soil age, suggesting that there has been significant weathering, chelation, and translocation of the parent material P (apatite) (Alexander and Burt, 1996).

Ca-bound P (195 to 49 mg kg^{-1}) and total P (700 to 300 mg kg^{-1}) decrease in E horizons relative to underlying horizons with soil age. Nonoccluded Al-P + Fe-P are not so consistent with soil age as Ca-P (Table 3). Occluded Fe-P and Al-P were very low and not measurable in any pedon. The relatively small amounts of Al-P + Fe-P are indicative of the low clay contents in these pedons (Alexander and Burt, 1996), especially in E horizons relative to the B and C horizons of the corresponding pedon. Clay functions as an adsorptive surface for P-retaining Fe-oxides. With the exception of the > 240-yr old pedon, the proportion of total P that is inorganic P (Ca-P + (Al-P + Fe-P)) decreases with soil age in B horizons. The organic P fraction may tend to comprise a greater proportion of the total P as organic matter accumulates with soil age.

Extractable or "available" P shows no trend with soil age but consistently decreases with depth within pedons (Table 3). Unlike the extractable bases which show a sharp decrease below O horizons, there is an accumulation of extractable P in the mineral surface horizons. Phosphorus has a slower recycling rate as it is tightly bound in most soils in a complex mixture of mineral and organic materials, and only a small fraction of the total soil P is considered plant available. The relative accumulation of extractable P



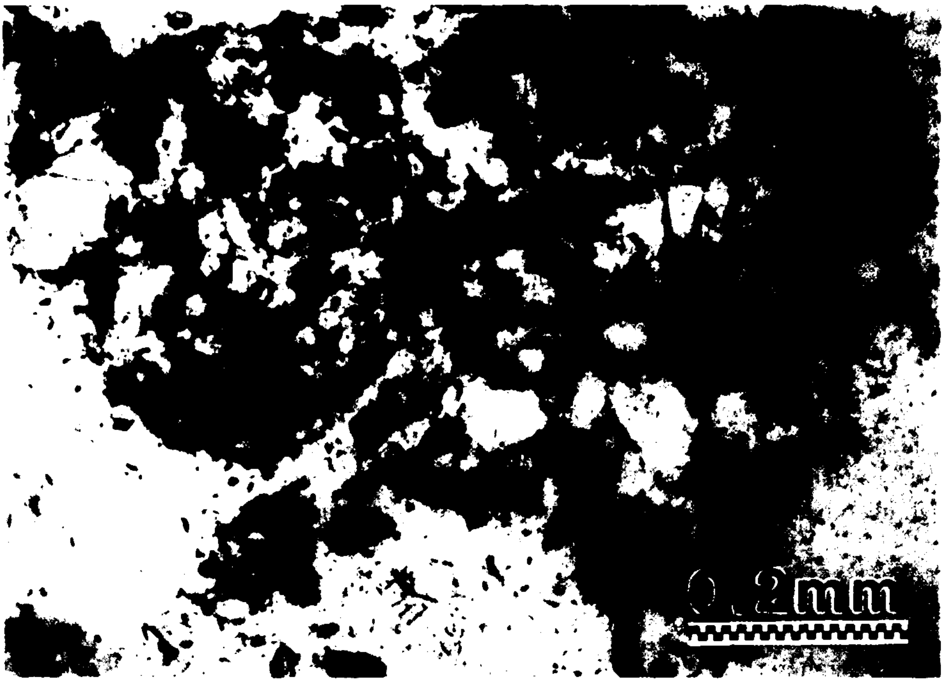


Fig. 4. Thin section photomicrograph of the BC horizon of the > 240-yr old pedon under plane polarized light showing Fe oxide deposits on mineral surfaces of very fine sand and silt-sized quarts, feldspar, and hornblende.

in mineral surface horizons does not parallel the distributions of either organically-bound Fe and Al (Fe_p, Al_p) or ferrihydrite (Fe_o) but rather mirrors organic matter distribution.

3.4. Micromorphology

Examination of natural fabric by SEM and optical microscopy provides a view of spodic horizon development with soil age. Soil textures range from sandy to coarse loamy (Alexander and Burt, 1996), which are typical of Spodosols (McKeague et al., 1983). The surface horizons of the younger pedons are predominantly aggregates of uncoated sand-sized grains with few organic constituents as evidenced in the A horizon of the 38-yr old pedon (Fig. 3A). Predominantly clean sand- and silt-size grains indicate that clay is generally an insignificant factor in development in these pedons. Early processes of eluviation are evidenced by the etching of mineral grains in the E horizon of the 70-yr old pedon (Fig. 3B).

Fig. 3. SEM photomicrograph of soil natural fabric: (A) relatively unetched or pitted silt-sized mineral grains with limited evidence of biological activity in the A horizon of the 38-yr old pedon; (B) linear etching and pitting of mineral grains in E horizon of 70-yr old pedon indicating initial weathering; (C) silt- and sand-sized grains of the Bs horizon of the 70-yr old pedon with small amounts of inorganic materials, likely translocated from overlying horizons; (D) silt-sized mineral grains of the BC horizon of the > 240-yr old pedon with an abundance of organic and inorganic constituents around grains indicating increased biological activity.

There are no cracked coatings or visible bridging between mineral grains in subsoil horizons of these pedons, but the fabric of the BC horizon of the oldest pedon (> 240 yr), which was described as brittle in the field (Alexander and Burt, 1996), appears primarily comprised of coarser mineral grains surrounded by a dense groundmass of finer material including humic materials. The BC horizon of the > 240-yr old pedon is the only horizon with optical evidence of Fe-oxide accumulation (Fig. 4).

As the amount of organic constituents and their distribution with depth increase with soil age, there is increased microbial and root activities as seen in the SEM photomicrographs of the Bs vs. BC horizons of the > 240-yr old pedons, respectively (Fig. 3C and D). Loose B horizons in Podzolic soils permeated by roots have been characterized by relatively intense biological activity with higher rates of C and N cycling (low C/N values), whereas cemented B horizons with no roots have been characterized almost exclusively by organo-mineral grain coatings, higher C/N ratios and a longer mean residence time for organic matter, indicating weaker biological activities than in loose B horizons (Page and Guillet, 1991). The overall loose consistency, low C/N ratios, and high microbial and root activity of these pedons signal their youth.

4. Summary and conclusions

This chronosequence study indicates that spodic development is achieved within a relatively short period of time. Accumulation and mineralization of organic matter is the dominant factor which results in development of E/Bs horizonation within 70 yr and the development of spodic horizons by 240 yr. The climate of southeast Alaska is favorable to rapid organic matter accumulation in soils. The increase in organic matter with soil age is directly responsible for development of many soil properties, e.g., CEC, acidity, 1500-kPa water retention, and variable charge.

Greater weathering intensity of E horizons relative to illuvial B horizons is indicated by both absolute and relative decreases in Ca-P and total P in E horizons, compared to underlying horizons. Free Fe oxides, predominately in the form of ferrihydrite, increasingly accumulate in the illuvial horizons with soils age. Evidence that in situ mineral weathering processes are contributing to increasing Fe oxide in subsoils exists only in the > 240-yr old pedon. Only in the oldest soil (> 240 yr) does evidence exist for a significant degree of in situ mineral weathering contributing to this free Fe increase in subsoils. These data suggest that the dominant process for Fe accumulation in these soils results from organic matter mineralization, which decreases pH, resulting in weathering of soil minerals and formation of fulvic-metal complexes which are readily eluviated to lower horizons in these sandy soils.

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