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Hornblende etching and quartz/feldspar ratios as weathering and soil development indicators in some Michigan soils

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Abstract

Weathering can be used as a highly effective relative age indicator. One such application involves etching of hornblende grains in soils. Etching increases with time (duration) and decreases with depth in soils and surficial sediments. Other variables, related to intensity of weathering and soil formation, are generally held as constant as possible so as to only minimally influence the time–etching relationship. Our study focuses on one of the variables usually held constant—climate—by examining hornblende etching and quartz/feldspar ratios in soils of similar age but varying degrees of development due to climatic factors. We examined the assumption that the degree of etching varies as a function of soil development, even in soils of similar age. The Spodosols we studied form a climate-mediated development sequence on a 13,000-yr-old outwash plain in Michigan. Their pedogenic development was compared to weathering-related data from the same soils. In general, soils data paralleled weathering data. Hornblende etching was most pronounced in the A and E horizons, and decreased rapidly with depth. Quartz/feldspar ratios showed similar but more variable trends. In the two most weakly developed soils, the Q/F ratio was nearly constant with depth, implying that this ratio may not be as effective a measure as are etching data for minimally weathered soils. Our data indicate that hornblende etching should not be used as a stand-alone relative age indicator, especially in young soils and in contexts where the degree of pedogenic variability on the geomorphic surface is large.

Keywords: Relative age dating; Soil development; Hornblende; Quartz/feldspar ratios; Surface exposure dating; Spodosols

Introduction

Hornblende is common in crystalline rocks (Blackburn and Dennen, 1988) and is the most abundant heavy mineral in many soils (Allen and Hajek, 1989; Blackburn and Dennen, 1988; Dreimanis et al., 1957; Dworkin et al., 1985; Hall and Martin, 1986). In soils, hornblende is most common in the sand and silt fractions (Allen and Hajek, 1989; Locke, 1979; Ruhe et al., 1966).

Weathering corrodes/etches hornblende minerals in a crystallographically controlled manner (Berner and Schott, 1982; Berner et al., 1980; Velbel, 1987, 1989). Etch pits form on the grain surface and progress through a sequence of stages, enlarging and coalescing with time (Berner and Schott, 1982; Berner et al., 1980; Cremeens et al., 1992; Lång, 2000). End-to-end coalescence results in the formation of longitudinal grooves or striations, whereas side-by-side coalescence forms denticulated or sawtooth margins (Fig. 1). Progressive weathering causes the etch features to systematically increase in amplitude and size (Berner and Schott, 1982; Locke, 1979, 1986; Velbel, 1993). Etching data has an advantage over other proxy data for weathering because it can be objectively obtained and is amenable to statistical analysis (Hall and Michaud,

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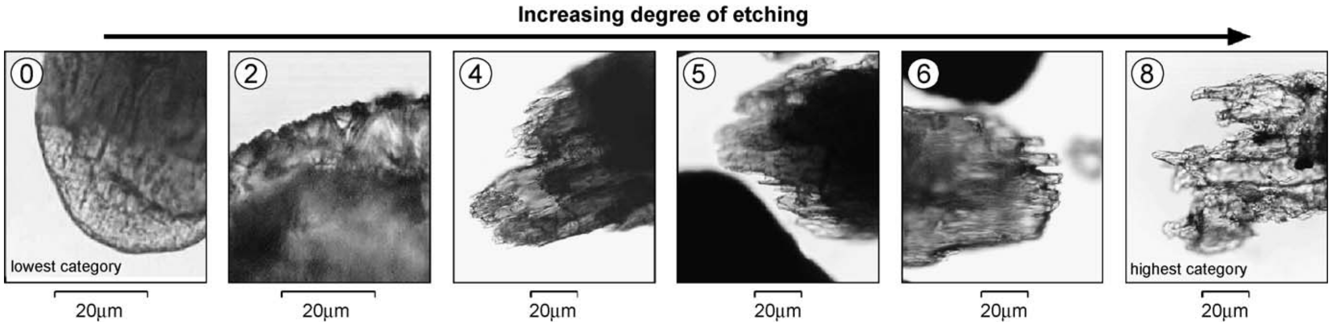

Figure 1. Examples of different degrees of etching in hornblende grains, illustrating some of the etching classes applied in this research.

1988). Like other weathering-related phenomena in soils, hornblende etching also varies in different climatic regimes (Hall and Horn, 1993).

Hornblende etching (HE) is greater in near-surface soil horizons, and usually decreases logarithmically with depth (Hall and Michaud, 1988; Lång, 2000; Locke, 1979, 1986), paralleling hornblende depletion data (April et al., 1986). Likewise, the depth of measurable etching is greater in older soils (Locke 1979). For this reason, HE has been applied as a relative age indicator in soils in, e.g., the Rocky Mountains (Hall and Martin, 1986; Hall and Michaud, 1988) and the Arctic (Locke, 1979, 1986). In these studies, the general approach involves relating aspects of hornblende denticulation, or etching amplitude, to surface age or exposure (Locke, 1979). Once this relationship has been established for surfaces of known age, it can, theoretically, be extrapolated to those of unknown age. Other factors, such as climate or relief, are usually held constant in these studies so that the effect of time on etching can be established. HE has been most commonly applied to soils and surfaces that are younger than 150,000 yr (Hall and Horn, 1993; Locke, 1986), suggesting that it is a sensitive weathering indicator on relatively young surfaces but on much older surfaces it is less discriminating than are other surface exposure dating methods. Locke's (1979) study applied HE to soils as old as 200,000 yr, but this was a periglacial region where soil formation and weathering are slow.

Another mineralogical indicator of weathering is the ratio of a resistant mineral (or minerals) to one (or more) that is more susceptible to weathering. The most common minerals used in this regard are quartz (Q) and feldspar (F) (Bockheim et al., 1996; Dorronsoro and Alonso, 1994; Muhs 1982; Nesbitt and Markovics, 1997; Ruhe, 1956). Like data on hornblende denticulation, Q/F ratios tend to decrease with depth in soils. Because Q/F ratios involve total depletion of a mineral rather than simple etching, it is perhaps slower to change than are other indices of weathering. Thus, Q/F ratios might be more applicable to soils and surfaces that are in moderate to advanced stages of weathering (Bockheim et al., 1996; Dorronsoro and Alonso, 1994; Muhs, 1982; Ruhe, 1956; Soller and Owens, 1991).

Because weathering processes are time-dependent, most hornblende etching studies have been set up such that *duration of surface exposure* is the primary factor influencing denticulation amplitude; similar statements could be made for studies involving Q/F ratios, e.g., Ruhe (1956), Locke (1979), and Hall and Michaud (1988). These studies have generally assumed that (1) etch features enlarge, and feldspars continue to be lost with time, and (2) the relationship is strong enough that it overwhelms any statistical "noise" introduced by, e.g., pH, moisture or leaching regime, water-holding capacity, organic matter content, or variations in hornblende mineralogy (White and Brantley, 1995). Because most of these studies have deliberately held climate relatively constant across the study sites, there exists little information about the effect of climate on these two weathering indicators, vis a vis time.

HE research has great potential as a surface exposure dating tool but is nonetheless still in its infancy, having been applied in only a few settings and circumstances. The literature associated with this tool has yet to determine the effect of weathering duration vs. intensity (as proxied by soil development and as mediated by climate) on etching. Our research, therefore, was designed to examine the relationship between mineral weathering in soils, as manifested in hornblende etch features and Q/F ratios, and surficial weathering intensity and duration, as proxied by soil development. Traditionally, these mineralogical measures have been applied to soils on surfaces of different age; time is allowed to vary and the mineralogical data are correlated to it. Our approach is somewhat different. We questioned the degree to which mineral-based measures are responding to duration vs. intensity of weathering (or soil development) and suggest that both must be considered. Therefore, in our study, we held time constant and allowed soil development/weathering to vary by examining four soils similar in age but with different profile morphologies—from very weakly to strongly developed Spodosols. In sum, the purpose of our study was to examine two mineralogical indicators of weathering, both of which have been used as relative age dating tools, on a surface of constant age but with varying degrees of soil development, to determine the sensitivity of these indicators to a factor other than time (or surface age), i.e., climate.

Study area

This study compiled data from four soils, all of which are located on a geomorphic surface associated with the Port Huron re-advance of the Laurentide ice sheet in northwestern lower Michigan (Fig. 2; Blewett and Winters, 1995). The Port Huron ice advanced to its farthest point in Michigan ca. 13,000 yr ago, forming a large head of outwash as it stagnated (Blewett, 1991; Blewett and Winters, 1995; Blewett et al., 1993). All soils are located on well-drained locations on this outwash apron in Kalkaska County, MI, which enabled us to hold surface/sediment age, drainage/wetness, and texture of the parent material relatively constant (Table 1).

The soils in this region, by virtue of their coarse textures, cool, snowy climate, and mixed coniferous–deciduous vegetation, are influenced by podzolization (Barrett and Schaetzl, 1992; Lundström et al., 2000; Messenger et al., 1972). In podzolization, infiltrating water containing dissolved organic acids drives translocation of Fe, Al, and organic carbon from E to Bhs and Bs horizons. Podzolization, which is especially strong in this region (Schaetzl and Isard, 1991), leads to the formation of soils that classify as Spodosols, with some variant on O-A-E-Bhs-Bs-BC-C horizonation. Any carbonates in the soil must be weathered and leached from the system before podzolization can proceed.

Within this region, even across short distances, there is a great deal of variability in macroclimate due to its location within the narrow but intense lake effect snowbelt of Lake Michigan (Norton and Bolsenga, 1993). Among the four study sites, the amount of snowfall is reasonably predictable: 4 > 3 > 2 > 1 (Fig. 2). Increased snowfall accentuates soil development and podzolization. More water infiltrates into the soil in snowbelt areas, facilitating weathering, leaching, and translocation of Fe, Al, and organic matter (Schaetzl and Isard, 1991, 1996). Additionally, soil under deep snow cover is less likely to freeze and thus stays permeable throughout the spring when podzolization is potentially intense (Isard and Schaetzl, 1995; Schaetzl and Isard, 1991).

Paralleling the snowfall gradient is a floristic trend, from open, xeric, fire-prone jack pine (*Pinus banksiana*) stand at site 1, to white (*Pinus strobus*) and red pine (*Pinus*

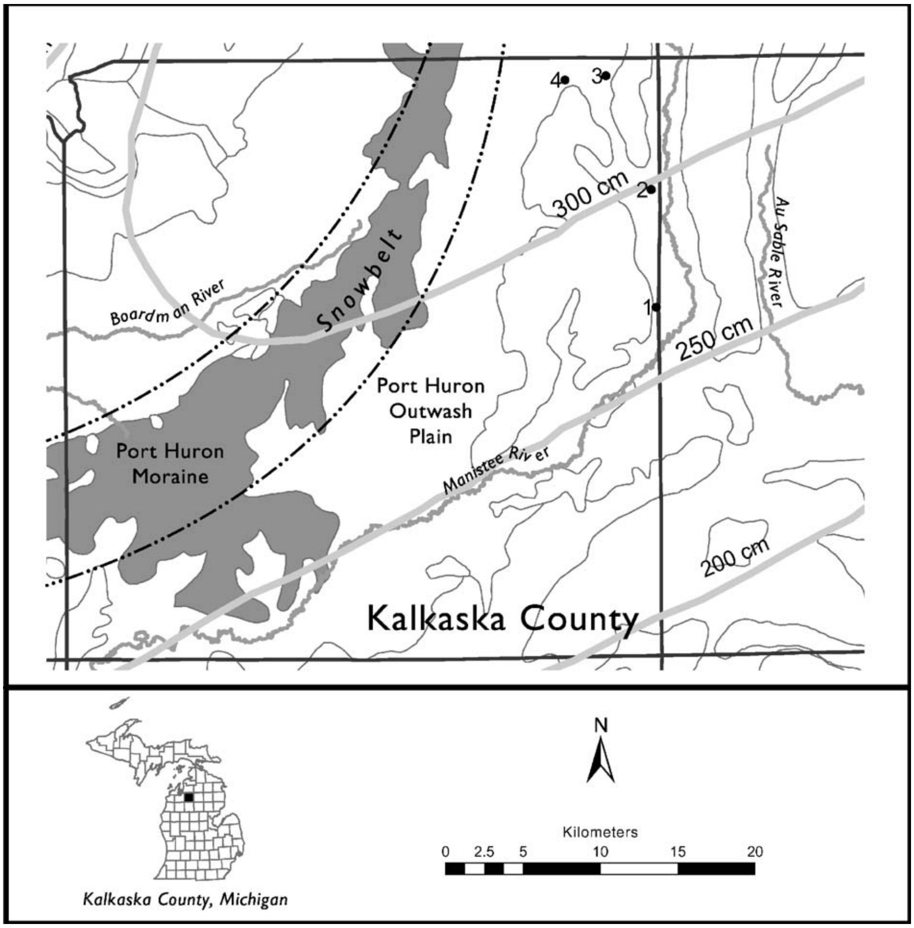

Figure 2. Study area map, showing the locations of the four soil pits and nearby landforms in northern Michigan. The various thin lines on the map reflect minor landform subdivisions, based on Farrand and Bell (1982). The dark gray polygon is the outer Port Huron moraine. The lake effect snowbelt is indicated by the thick, gray isolines of mean annual snowfall totals, after data in Eichenlaub et al. (1990). Site numbers refer to these site names used in the text: 1—Grayling; 2—Weak Rubicon; 3—Strong Rubicon; 4—Kalkaska.

Table 1
Physical, chemical, and morphological data for the four soils studied

Horizon	Depth (cm)	Munsell color (moist)	pH (2:1 soil/water)	Coarse fragments (>2-mm diameter) (estimated volume percent of whole sample)	Sand (%)	Silt (%)	Clay (%)	Texture class[a]	Mean particle size (μm)
Kalkaska (site 4 on Fig. 2) USPLS location: SE 1/4, NE 1/4, Sec. 5, T28N, R5W									
Oi	0–3	–		0					
A	3–16	7.5YR 2/0	4.7	0	88.3	11.6	0.0	S	345
E	16–24	5YR 4/3	4.2	0	87.5	12.4	0.0	S	359
Bhs	24–31	5YR 2.5/2	4.0	0	83.3	13.2	3.5	LS	340
Bs1	31–58	7.5YR 4/6	6.1	0	95.1	4.9	0.0	S	355
Bs2	58–85	5YR 5/8	6.6	4	97.4	2.5	0.0	S	413
Bw	85–128	10YR 4/6	6.7	4	98.2	1.8	0.0	S	343
2E/Bt	128–160+	10YR 4/6 (E) 7.5YR 4/4 (Bt)	6.9	8	98.1	2.0	0.0	S	384
Strong Rubicon (site 3 on Fig. 2) USPLS location: SW 1/4, NE 1/4, Sec. 3, T28N, R5W									
Oi	0–5	–		0					
A	5–9	7.5YR 3/2	5.4	2	90.3	9.7	0.0	S	364
E	9–18	7.5YR 4/2	6.1	2	90.3	8.2	1.4	S	363
Bs1	18–28	5YR 4/6	5.7	6	90.5	8.8	0.7	S	374
Bs2	28–48	7.5YR 4/6	6.4	6	93.5	6.5	0.0	S	362
BC	48–79	10YR 5/6	7.1	8	98.1	2.0	0.0	S	422
C	79–170+	10YR 6/4	7.2	8	98.6	1.4	0.0	S	391
Weak Rubicon (site 2 on Fig. 2) USPLS location: NW 1/4, SE 1/4, Sec. 36, T28N, R5W									
Oi	0–4	–		0					
A	4–9	N 2/0	4.0	0	96.8	3.3	0.0	S	421
E	9–20	7.5YR 4/2	6.1	0	95.1	3.7	1.2	S	401
Bs1	20–41	5YR 3/4	6.1	0	95.3	4.8	0.0	S	389
Bs2	41–62	10YR 4/6	6.9	0	98.8	0.1	1.0	S	378
BC	62–126	10YR 5/4	7.2	1	99.6	0.5	0.0	S	323
C	126–165+	10YR 6/4	7.5	1	99.7	0.0	0.4	S	291
Grayling (site 1 on Fig. 2) USPLS location: NW 1/4, NW 1/4, Sec. 30, T27N, R4W									
Oi	0–7	–		0					
A	7–11	7.5YR 3/2	4.4	0	91.0	9.0	0.0	S	364
Bs	11–36	7.5YR 4/6	6.1	0	96.4	3.6	0.0	S	386
BC	36–62	10YR 5/6	6.9	0	99.4	0.7	0.0	S	409
C	62–116	10YR 5/4	7.2	2	99.6	0.4	0.0	S	406
2C	116–140	10YR 5/3	7.2	6	98.9	1.1	0.0	S	409
3C	140–165+	10YR 5/3	7.3	0	99.4	0.6	0.0	S	369

[a] S: sand, LS: loamy sand. Textures according to the Soil Survey Division Staff (1993).

resinosa) stands at sites 2 and 3, to a northern hardwood stand with sugar maple (*Acer sachharum*), white pine, hemlock (*Tsuga canadensis*), and yellow birch (*Betula allegeniensis*) at site 4. Thus, it is difficult to separate vegetation and climate as independent variables, for they interact so closely (Mokma and Vance, 1989; Schaetzl, 2002).

Methods

Study sites were chosen based on criteria intended to constrain the state factors of relief/topography, parent material, and time (Jenny, 1941). All are on the Port Huron outwash surface, which dates to ca. 13,000 yr ago (Blewett et al., 1993). Additionally, all are on nearly level, well-drained locations, far from any escarpments or topographic “edges” that might affect subsurface or surface water movement. The remaining two factors (climate and organisms) vary among the sites and are strongly correlated to each other, even across short distances (Schaetzl, 2002).

Using these criteria, four sites that span the range of pedogenic expression/development on the outwash surface, but are representative of broad areas of the surface, were chosen for sampling (Fig. 2). We emphasize that the soils at these four sites span over 90% of this part of the Port Huron outwash plain, and are therefore highly representative of that geomorphic surface. The soil at site 4 classifies within the Kalkaska series (Typic Haplorthods); it is the best developed soil of the four. Sites 2 and 3 both are within the intermediately developed Rubicon series (Entic Haplorthods), but the soil at site 3 was better developed (Table 1), and thus we named sites 2 and 3 “Weak Rubicon” and “Strong Rubicon,” respectively. The weakest soil development in the region is an area mapped as a consociation of Grayling (Typic Udipsamments) soils; this was our site 1. Although the soil sampled here was morphologically similar to other Grayling soils in the region, it (surprisingly) met all the criteria for a weakly developed Spodosol (Entic Haplorthod). For the sake of communication, however, we will refer to this pedon as Grayling; it would undoubtedly be remapped in the Grayling series by NRCS personnel.

At each site, a backhoe pit was opened and the soil profile described according to standard procedures (Soil Survey Division Staff, 1993). Samples of about 4 kg were taken from the profile face, for each genetic horizon, and air-dried. We also augered an additional meter below the bottom of each pit, and sampled the unaltered C horizon material from that depth; these samples have the prefix “Deep” in subsequent figures and tables. Coarse fragments (>2-mm diameter) were removed by sieving. Two passes through a sample splitter resulted in a well-mixed, 1-kg sample, which was used for subsequent analyses. Soil pH (2:1 soil/water) was measured with a model #720A Orion pH meter. Particle size analysis was performed by pipette (Soil Survey Laboratory Staff 1996). During the pipette analysis, the fine sand fraction (125–250-μm diameter) was captured and placed in a bath of 3% sodium hypochlorite (NaOCl) to remove organic matter, followed by a water rinse and oven drying. The heavy fraction of the fine sand was separated using a sodium polytungstate solution at a specific gravity of 2.95 g cm^3. Because hornblende has a specific gravity of 2.9–3.3 (Blackburn and Dennen, 1988), it sank to the bottom of the separatory funnel and was extracted. Three hundred hornblende grains from each horizon were measured and the amplitude of the denticulated, teeth-like margins for each grain were determined under a petrographic microscope at 200×; we choose a sample size of 300 because it provides adequate confidence limits (Mikesell, 2002; Van der Plas and Tobi, 1965). To ascertain the degree of HE precisely, we directly measured denticulation amplitudes at the margins of the grains with a graded ocular. The maximum denticulation amplitude of each grain was used to assigned it to a class based on the scheme of Locke (1979). Classes ranged from 0 to 8 with class breaks every 4 μm; grains that showed no apparent etching were assigned to Class 0 and the most severely denticulated grains were in Class 8 (Fig. 1).

A second index of weathering, the quartz/feldspar (Q/F) ratio, was calculated for the fine sand fraction of each horizon. Grain samples were placed in a container and impregnated with epoxy resin. Thin sections were then cut, acid-etched, and stained with Alizarin red to help distinguish plagioclase from quartz. Exactly 300 grains per horizon were then counted under a petrographic microscope. Plagioclase and K-feldspar counts were summed to arrive at a count of all feldspars.

Because podzolization is expressed chemically as illuvial coatings on grains, we wanted to know the types and amounts of Fe and Al compounds in our soil samples (McKeague, 1967; McKeague and Day, 1966; Parfitt and Childs, 1988). Thus, A, E, and B horizon samples were exposed to three extractants: sodium citrate–dithionite (CD), acidified ammonium-oxalate (AAO), and sodium pyrophosphate (PP) (Loeppert and Inskeep, 1996; Ross and Wang, 1993). CD primarily extracts “free” Fe and Al, denoted by Fe_d and Al_d, from pedogenic oxide minerals (Jackson et al., 1986). AAO extracts “active” Fe and Al (Fe_o and Al_o) from noncrystalline hydrous oxides. The term “active” is given to oxides that are small in size, have a high surface area, and a high degree of reactivity (Loeppert and Inskeep, 1996). PP extracts Fe and Al (Fe_p and Al_p) from organically bound complexes and, to a lesser degree, noncrystalline hydrous oxides. The supernatants were analyzed on the flame apparatus of a Perkin-Elmer 5100 PC AAS (Soil Survey Laboratory Staff, 1996).

Results and discussion

The four soils, all of which classified as Spodosols, have formed in nearly uniform sands, with all but one horizon in the “sand” texture class (Soil Survey Division Staff, 1993; Table 1). Medium sand dominated the five sand fractions. Mean particle size data for the soils were typically in the 320–420-μm range, in the medium sand (250–500 μm) fraction (Table 1). No horizon had more than 3.5% clay and the majority had no measurable clay. Thus, we assumed that variation in degree of pedogenesis and weathering among the soils is probably due to factors other than variation in parent material. For example, the soils had minimal silt contents at depth, in the parent material. However, they all also had a significant silt peak, ranging from 3.6 to >10%, in their upper sola, which we interpreted as reflecting either a slight eolian influx or additions due to weathering (Table 1).

Pedogenic development vs. weathering indicators

To evaluate the effects of time vs. weathering/soil development, we first had to evaluate the varying degrees of soil development that exist on this outwash surface, as exemplified by the four soils. Table 2 illustrates and ranks various pedogenic development data for the soils, and shows that:

Kalkaska>Strong Rubicon>Weak Rubicon>Grayling

Soil development on the Port Huron outwash surface parallels snowfall patterns (Fig. 2). The best developed soil (Kalkaska) is located nearest the heart of the snowbelt while the weakest soil (Grayling) is farthest inland, away from the snowbelt; this is the typical macroclimate–pedogenic relationship for the northern Great Lakes region (Schaetzl,

Table 2
Pedogenesis and weathering indicators, ranked for the four soils studied

Criterion of comparison[a]	Grayling (site 1)	Weak Rubicon (site 2)	Strong Rubicon (site 3)	Kalkaska (site 4)
Pedogenesis indicators				
Solum thickness (cm)	62 (2)	62 (2)	48 (4)	128 (1)
E horizon thickness (cm)	0 (4)	11 (1)	9 (2)	8 (3)
B horizon thickness (cm)	25 (4)	42 (2)	30 (3)	61 (1)
POD Index[b]	0 (3)	2 (1)	0 (3)	1.5 (2)
A or E horizon pH (lowest of the two)	4.4 (3)	4.0 (1)	5.4 (4)	4.2 (2)
B horizon pH (lowest of any subhorizon)	6.1 (3)	6.1 (3)	5.7 (2)	4.0 (1)
Hue of reddest B horizon	7.5YR (4)	5YR (1)	5YR (1)	5YR (1)
Color value of darkest B horizon	4 (3)	3 (2)	4 (3)	2.5 (1)
Citrate-dithionite-extractable Fe in Bs and Bhs horizons (%), weighted (multiplied) by B horizon thickness (cm)	2.75 (4)	7.14 (3)	13.60 (1)	10.92 (2)
Pyrophosphate-extractable Fe in Bs and Bhs horizons (%), weighted (multiplied) by B horizon thickness (cm)	1.75 (3)	1.68 (4)	4.20 (1)	3.89 (2)
Oxalate-extractable Fe in Bs and Bhs horizons (%), weighted (multiplied) by B horizon thickness (cm)	0.75 (4)	1.47 (3)	3.30 (1)	2.88 (2)
Citrate-dithionite-extractable Al in Bs and Bhs horizons (%), weighted (multiplied) by B horizon thickness (cm)	2.75 (4)	5.04 (3)	6.20 (2)	7.53 (1)
Oxalate-extractable Al in Bs and Bhs horizons (%), weighted (multiplied) by B horizon thickness (cm)	4.76 (4)	7.77 (3)	8.60 (2)	9.62 (1)
Overall mean rank for pedogenesis	3.4	2.2	2.2	1.9
Overall median rank for pedogenesis	4	2	2	1
Weathering indicators				
Hornblende denticulation[c] (categories 0–8, with 0 being lowest), weighted profile mean	1.19 (4)	1.38 (3)	1.66 (2)	2.59 (1)
Hornblende denticulation, profile maximum (category)	3.24 (4)	5.79 (3)	7.16 (2)	8.21 (1)
Hornblende denticulation, profile minimum (category)	0.39 (4)	0.57 (3)	1.15 (2)	1.31 (1)
Hornblende denticulation at 50-cm depth (mean of categories)	1.75 (4)	2.04 (2)	1.77 (3)	2.79 (1)
Q/F ratio, weighted profile mean	8.49 (2)	5.66 (4)	9.49 (1)	8.37 (3)
Q/F ratio, profile maximum	10.5 (3)	7.8 (4)	24.0 (1)	16.7 (2)
Q/F ratio, profile minimum	5.3 (3)	4.6 (4)	6.1 (2)	6.3 (1)
Silt content in A horizon (%)	9.0 (3)	3.3 (4)	9.7 (2)	11.6 (1)
Silt content: maximum in any near-surface horizon (%)	9.0 (3)	4.8 (4)	9.7 (2)	13.2 (1)
Overall mean rank for weathering	3.3	3.4	1.9	1.3
Overall median rank for weathering	3	4	2	1

[a] Numbers in parentheses represent the rank for the variable in question, with 1 being maximum and 4 being minimum.

[b] The POD Index (Schaetzl and Mokma, 1988) is a field-based index of podzolization; higher values indicate increased soil development.

[c] Denticulation categories are defined in the text. They range from 0 to 8, with 0 being lowest; see Figure 1.

2002; Schaetzl and Isard, 1996). The two Rubicon soils were comparable in development, both having a mean rank of 2.2 and a median rank of 2 (Table 2). In the field, however, it was clear that the one Rubicon pedon—"Strong Rubicon"—was better developed, with a more chemically and morphologically contrasting E–B sequum, along with an increased amount of ortstein (Bsm material). The Strong Rubicon site was closer to the core of the snowbelt than was

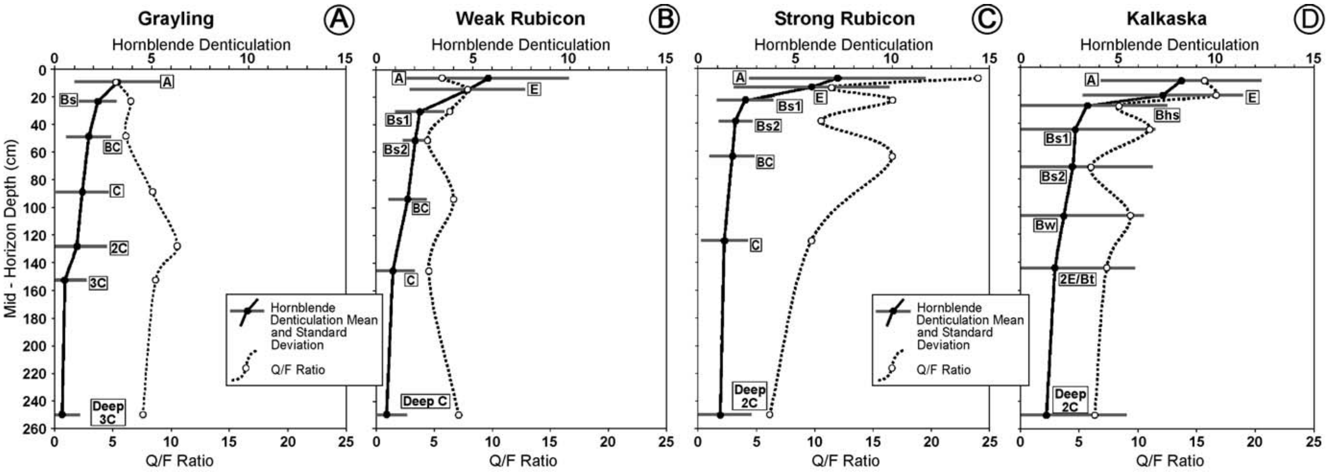

Figure 3. Depth plots of mean hornblende etching amplitudes and Q/F ratios for each of the four soils, by horizon. Units on the hornblende denticulation axis are discussed in the text; classes range from 0 (lowest) to 8 (highest).

the Weak Rubicon site. Thus, it is clear that soil development can and does vary significantly, but predictably, on this geomorphic surface.

Once we had established the relative amount of soil development, we compared the pedogenic data with weathering-related parameters. We assumed that weathering trends would parallel pedogenic trends. Table 2 illustrates and ranks various weathering-related data for the soils, and shows that:

Kalkaska>Strong Rubicon>Grayling>Weak Rubicon

The only difference between the weathering and pedogenic data is that the Grayling and Weak Rubicon pedons were switched in rank (Table 2). The weathering data also indicated that despite the similar (and relatively young) age of all the soils, the magnitude of their weathering-related differences was quite large (Table 2).

Hornblende denticulation and Q/F ratios

Hornblende grains were significantly more weathered, as determined by denticulation amplitudes, at the top of the soil profile than at the bottom, at all four sites (Figs. 3, 4). In every case, the largest denticulation amplitudes were in the uppermost horizon and etching was minimal in the deepest C horizon. This pattern was so closely aligned with pH data that it appears pH is a driver for etching of hornblende grains in these soils (Fig. 5). These data also support Hall

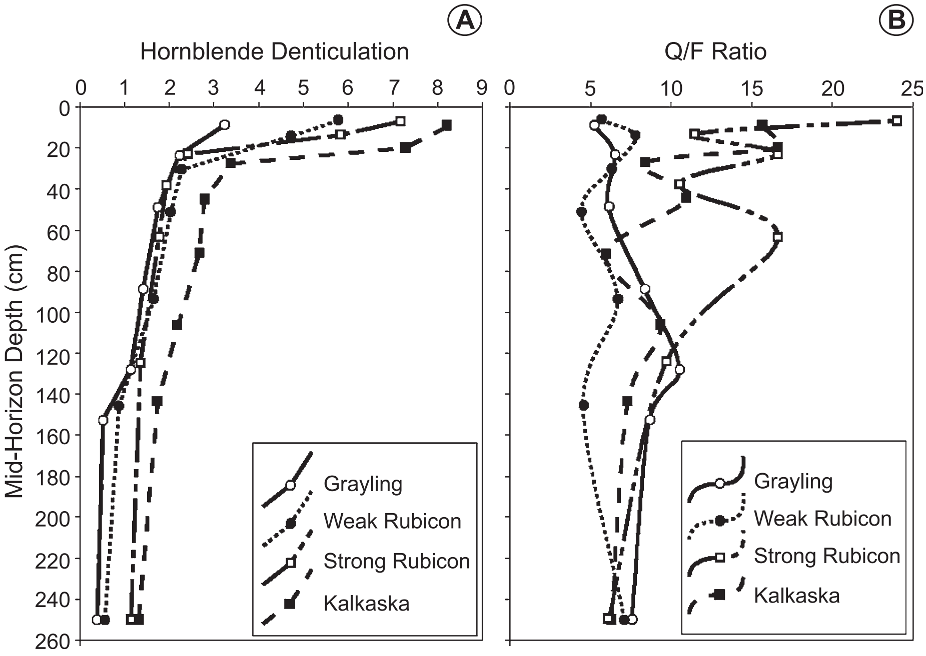

Figure 4. Comparisons of (A) mean hornblende etching amplitudes and (B) Q/F ratios for each of the four soils. Units on the hornblende denticulation axis are discussed in the text; classes range from 0 (lowest) to 8 (highest).

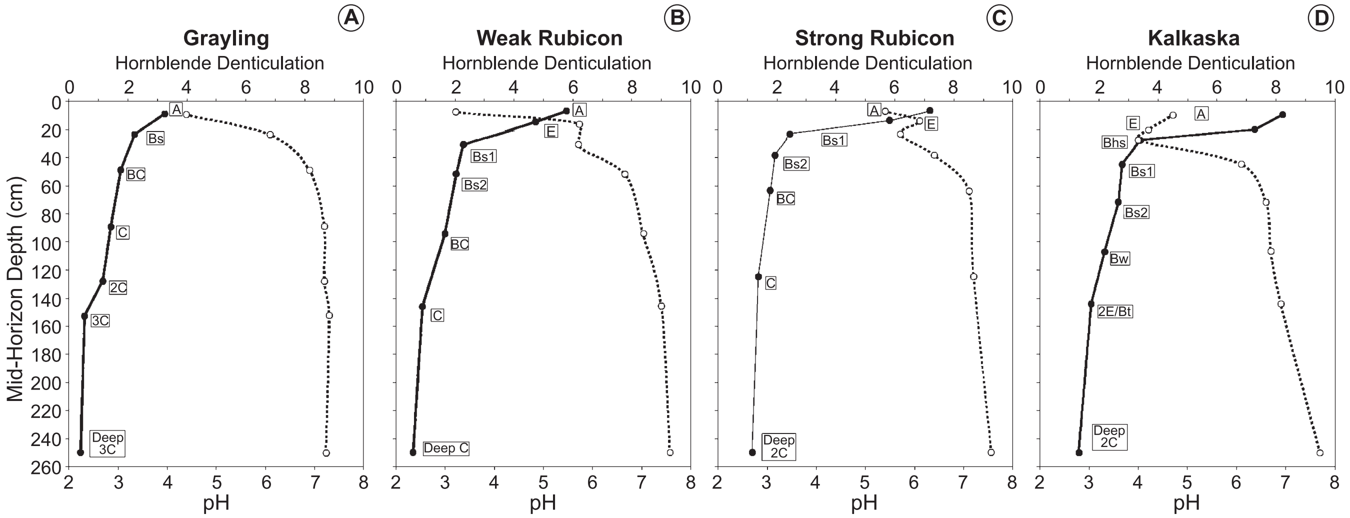

Figure 5. Depth plots of mean hornblende etching amplitudes and pH for each of the four soils, by horizon. Units on the hornblende denticulation axis are discussed in the text; classes range from 0 (lowest) to 8 (highest).

and Horn's (1993) conclusion that etching, particularly at shallow depths, is rapid within the first 10,000–15,000 yr of soil formation. They also mirror data from Hall and Martin (1986), for soils in the Tobacco Root Range of Montana. The current climate in this alpine area is only slightly wetter than at our Michigan sites; soils at lower elevations are also slightly warmer. Nonetheless, Hall and Martin's data for the soils show, as do our data, logarithmically decreasing etching values with depth; the shape of their curves is remarkably similar to those shown in Figure 3. The main exception is that our Michigan soils, perhaps due to their lower pH values in the upper profile, exhibit stronger etching in the topmost horizons.

Standard deviations of the HE data are largest in the A horizon and get progressively smaller with depth (Fig. 3). We suggest that our denticulation data are excellent surrogates for weathering because, despite the wide degree of difference among the four soils in their upper sola, all soils have roughly similar values in their C horizons (Fig. 4). In soils where age is markedly different, HE data can be widely disparate, even at depth (Locke 1979). Our C horizon denticulation data also attest to the uniformity of parent materials among the sites.

Etching was generally much larger in A and E horizons than in horizons below, giving the depth trends for denticulation amplitude a distinct "break in slope" between the eluvial (A and E) and illuvial (B) parts of the profile (Fig. 4). This depth trend is different than the steady, logarithmically decreasing weathering intensity that has been reported elsewhere (Hall and Horn, 1993; Locke, 1979). We suggest that our etching data reflect the two-compartment pedogenic model reported by Ugolini et al. (1977). They monitored podzolization by sampling soil solutions in situ and documented the existence of an upper, *biopedological compartment* (the O, A, E, and upper B horizons) in which ionic movement is governed by soluble organic acids that depress the bicarbonate concentration. Most of these acids get captured and neutralized in the upper B horizon, leading to a rise in pH. In the lower, *geochemical compartment*, higher pH values lead to a weathering environment dominated by the dissociation of carbonic acid, increasing the importance of the bicarbonate ion in this part of the soil. Our HE data (Fig. 4) support the notion of two separate compartments of not only pedogenesis, but also weathering, in these young soils.

Hornblende etching (HE) data generally paralleled soil development data. The largest denticulation amplitudes occurred in the Kalkaska soil (pit 4) while the smallest amount of etching was observed in the weakly developed Grayling soil (Table 2). This pattern parallels that of snowfall and infiltration (Fig. 2), which supports the contention that, after the effect of age, soil moisture and depth of wetting are the most important factors in determining etching rates (Hall and Horn, 1993; Lång, 2000; Locke, 1979, 1986).

Q/F data were more variable than HE data, but suggested that the two best-developed soils (Kalkaska and Strong Rubicon) were more weathered than the Weak Rubicon and Grayling soils (Table 2). That is, instead of a clear, four-part sequence, as observed with the denticulation data, the soils broke out into two groups based on Q/F data (Fig. 4; Table 2). In the two more weakly developed soils, Q/F ratios were nearly constant with depth, implying that this method may not be as effective as HE for young and/or minimally weathered soils (Fig. 4). That is, if weathering intensity decreases steadily with depth, then this characteristic appears to be captured more precisely (in these young soils) by etching of hornblende than by loss of feldspar grains. Applications of HE in the literature seem to support this contention; most studies have applied HE to surfaces that are less than 150,000 yr old (Hall and Horn, 1993;

Locke, 1979, 1986). It has even been used with success on surfaces as young as 2500 yr (Hall and Horn, 1993; Hall and Martin, 1986; Hall and Michaud, 1988). On older soils, hornblende will be nearly or totally depleted in near-surface horizons, rendering it less useful or even meaningless. In that case, Q/F ratios may be better at assessing the degree of weathering in the older soils (Ruhe 1956). Again, the literature seems to support this conclusion; Q/F ratios in soils have been successfully applied on surfaces that are older than 200,000 yr (Bockheim et al., 1996; Dorronsoro and Alonso, 1994; Muhs, 1982; Ruhe, 1956). However, only rarely have Q/F ratios been used successfully on surfaces younger than 6 ka (Ruhe, 1956). Lastly, Q/F ratios are also useful in confirming consistency of parent material, as shown in the C horizon Q/F data in Figure 4.

Implications for surface exposure dating

The large variation in pedogenic and weathering data among the four soils—all of which are the same age—emphasizes that variation can and does occur in both of these parameters on a single geomorphic surface. Even more dramatic is the fact that this variation has occurred in only 13,000 yr. Barrett and Schaetzl (1993) showed that soil spatial variability appears to increase with time; they examined soils in Michigan that ranged in age from 3000 to 11,000 yr. We suspect that the divergence in the Q/F and HE data could and probably will get even greater with time, suggesting that these two weathering-related parameters be used with caution in surface exposure dating studies. As a minimum, age assessments for surfaces of different age, based on this type of data, must be taken from samples that were acquired at the same depth, and we would suggest, at a depth that is within the lower profile. Locke's (1979) data showed that variation in HE data can occur at depth, for soils of different age, and our data illustrate the fact that even when soils are of variable development, if they are of the same age their HE data are roughly comparable within the lower part of the profile (Fig. 4).

Hornblende etching is a surface exposure dating tool that has a great deal of promise in many different settings (Hall and Martin, 1986; Hall and Michaud, 1988; Locke, 1979). When compared to other dating tools, however, it has been studied and applied only minimally. Our study, hopefully, adds to the base of knowledge about this process and the various factors that govern it. Based on our data, we suggest that, when hornblende etching is used as a surface-age dating tool, care be taken to insure that other state factors, e.g., climate, vegetation, be held constant across each surface. If these other factors vary greatly, and only the investigator can know the amount of tolerance to allow, HE data within surfaces might be so strongly influenced that intersurface comparisons are meaningless, or in need of other supporting data. Additionally, HE data should derive from locations on surfaces where soil development is not "abnormally" strong or weak. Lastly, we agree with Hall and Michaud's (1988) conclusion that a multiparameter approach is the best strategy in relative-age dating studies, of which HE can be a useful and valuable component.

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References

Allen, B.L., Hajek, B.F., 1989. Mineral occurrence in soil environments. In: Dixon, J.B., Weed, S.B. (Eds.), Minerals in Soil Environments, (second ed.). Soil Science Society of America, vol. 1. Soil Science Society of America, Madison, WI, pp. 199–264.

April, R., Newton, R., Coles, L.T., 1986. Chemical weathering in two Adirondack watersheds: past and present-day rates. Geological Society of America Bulletin 97, 1232–1238.

Barrett, L.R., Schaetzl, R.J., 1992. An examination of podzolization near Lake Michigan using chronofunctions. Canadian Journal of Soil Science 72, 527–541.

Barrett, L.R., Schaetzl, R.J., 1993. Soil development and spatial variability on geomorphic surfaces of different age. Physical Geography 14, 39–55.

Berner, R.A., Schott, J., 1982. Mechanism of pyroxene and amphibole weathering: II. Observations of soil grains. American Journal of Science 282, 1214–1231.

Berner, R.A., Sjöberg, E.L., Velbel, M.A., Krom, M.D., 1980. Dissolution of pyroxenes and amphiboles during weathering. Science 207, 1205–1206.

Blackburn, W.H., Dennen, W.H., 1988. Principles of Mineralogy. Wm.C. Brown Publishers, Dubuque, IA. 413 pp.

Blewett, W.L., 1991. Characteristics, correlations, and refinement of Leverett and Taylor's Port Huron Moraine in Michigan. East Lakes Geography 26, 52–60.

Blewett, W.L., Winters, H.A., 1995. The importance of glaciofluvial features within Michigan's Port Huron moraine. Annals of the Association of America Geographers 85, 306–319.

Blewett, W.L., Winters, H.A., Rieck, R.L., 1993. New age control on the Port Huron moraine in northern Michigan. Physical Geography 14, 131–138.

Bockheim, J.G., Marshal, J.G., Kelsey, H.M., 1996. Soil-forming processes and rates on uplifted marine terraces in southwestern Oregon, USA. Geoderma 73, 39–62.

Cremeens, D.L., Darmody, R.G., Norton, L.D., 1992. Etch-pit size and shape distribution on orthoclase and pyriboles in a loess catena. Geochimica et Cosmochimica Acta 56, 3423–3434.

Dorronsoro, C., Alonso, P., 1994. Chronosequence in Almar River fluvial-terrace soil. Soil Science Society of America Journal 58, 910–925.

Dreimanis, G.H., Reavely, G.H., Cook, R.J.B., Knox, K.S., Moretti, F.J., 1957. Heavy mineral studies in till of Ontario and adjacent areas. Journal of Sedimentary Petrology 27, 148–161.

Dworkin, S.I., Larson, G.J., Monaghan, G.W., 1985. Late Wisconsinan ice-flow reconstruction for the central Great Lakes region. Canadian Journal of Earth Science 22, 935–940.

Eichenlaub, V.L., Harman, J.R., Nurnberger, F.V., Stolle, H.J., 1990. The Climatic Atlas of Michigan. Univ. Notre Dame Press, Notre Dame, IN. 165 pp.

Farrand, W.R., Bell, D.L., 1982. Quaternary Geology (map) of Southern Michigan with surface water drainage divides. 1:500,000 scale. Department of Natural Resources, Geol. Survey Division, Lansing, MI.

Hall, R.D., Horn, L.L., 1993. Rates of hornblende etching in soils in glacial deposits of the northern Rocky Mountains (Wyoming–Montana, U.S.A.): influence of climate and characteristics of the parent material. Chemical Geology 105, 17–29.

Hall, R.D., Martin, R.E., 1986. The etching of hornblende grains in the matrix of alpine tills and periglacial deposits. In: Colman, S.M., Dethier, D.P. (Eds.), Rates of Chemical Weathering of Rocks and Minerals. Academic Press, Inc., Orlando, FL, pp. 101–128.

Hall, R.D., Michaud, D., 1988. The use of hornblende etching, clast weathering, and soils to date alpine glacial and periglacial deposits: a study from southwestern Montana. Geological Society of America Bulletin 100, 458–467.

Isard, S.A., Schaetzl, R.J., 1995. Estimating soil temperatures and frost in the lake effect snowbelt region, Michigan, USA. Cold Regions Science Techology 23, 317–332.

Jackson, M.L., Lim, C.H., Zelazny, L.W., 1986. Oxides, hydroxides, and aluminosilicates. In: Klute, A. (Ed.), Methods of Soil Analysis: Part 1. Physical and Mineralogical Methods, SSSA Book Series, vol. 9(1). SSSA and ASA, Madison, WI, pp. 101–150.

Jenny, H., 1941. Factors of Soil Formation. McGraw-Hill, New York, NY. 281 pp.

Lång, L.-O., 2000. Heavy mineral weathering under acidic soil conditions. Applied Geochemistry 15, 415–423.

Locke III, W.W., 1979. Etching of hornblende grains in Arctic soils: an indicator of relative age and paleoclimate. Quaternary Research 11, 197–212.

Locke III, W.W., 1986. Rates of hornblende etching in soils on glacial deposits, Baffin Island, Canada. In: Colman, S.M., Dethier, D.P. (Eds.), Rates of Chemical Weathering of Rocks and Minerals. Academic Press, Orlando, FL, pp. 129–145.

Loeppert, R.H., Inskeep, W.P., 1996. Iron. In: Bartels, J.M. (Ed.), Methods of Soil Analysis. Part 3. Chemical Methods, SSSA Book Series, vol. 5(3). SSSA and ASA, Madison, WI, pp. 639–663.

Lundström, U.S., van Breemen, N., Bain, N., 2000. The podzolization process: a review. Geoderma 94, 91–107.

McKeague, J.A., 1967. An evaluation of 0.1 M pyrophosphate and pyrophosphate–dithionite in comparison with oxalate as extractants of the accumulation products in podzols and some other soils. Canadian Journal of Soil Science 47, 95–99.

McKeague, J.A., Day, J.H., 1966. Dithionite- and oxalate-extractable Fe and Al as aids in differentiating various classes of soils. Canadian Journal of Soil Science 46, 13–22.

Messenger, A.S., Whiteside, E.P., Wolcott, A.R., 1972. Climate, time, and organisms in relation to Podzol development in Michigan sands: I. Site descriptions and microbiological observations. Soil Science Society of America Proceedings 36, 633–638.

Mikesell, L.R., 2002. Hornblende etching as an indicator of soil development and relative weathering among Spodosols. MS thesis, Michigan State University.

Mokma, D.L., Vance, G.F., 1989. Forest vegetation and origin of some spodic horizons, Michigan. Geoderma 43, 311–324.

Muhs, D.R., 1982. A soil chronosequence on Quaternary marine terraces, San Clemente Island, California. Geoderma 28, 257–283.

Nebsitt, H.W., Markovics, G., 1997. Weathering of granodioritic crust, long-term storage of elements in weathering profiles, and petrogenesis of siliciclastic sediments. Geochimica et Cosmochimica Acta 61, 1653–1670.

Norton, D.C., Bolsenga, S.J., 1993. Spatiotemporal trends in lake effect and continental snowfall in the Laurentian Great Lakes, 1951–1980. Journal of Climate 6, 1943–1956.

Parfitt, R.L., Childs, C.W., 1988. Estimation of forms of Fe and Al: a review, and analysis of contrasting soils by dissolution and Moessbauer methods. Australian Journal of Soil Research 26, 121–144.

Ross, G.J., Wang, C., 1993. Extractable Al, Fe, Mn, and Si. In: Carter, M.R. (Ed.), Soil Sampling and Methods of Analysis. Canadian Society of Soil Science, Boca Raton, FL, pp. 239–246.

Ruhe, R.V., 1956. Geomorphic surfaces and the nature of soils. Soil Science 82, 441–455.

Ruhe, R.V., Daniels, R.B., Cady, J.G., 1966. Landscape evolution and soil formation in southwestern Iowa. Technical Bulletin-United States Department of Agriculture 1349. 242 pp.

Schaetzl, R.J., 2002. A Spodosol–Entisol transition in northern Michigan: climate or vegetation? Soil Science Society of America Journal 66, 1272–1284.

Schaetzl, R.J., Isard, S.A., 1991. The distribution of spodosol soils in southern Michigan: a climatic interpretation. Annals of the Association of American Geographers 81, 425–442.

Schaetzl, R.J., Isard, S.A., 1996. Regional-scale relationships between climate and strength of podzolization in the Great Lakes region, North America. Catena 28, 47–69.

Schaetzl, R.J., Mokma, D.L., 1988. A numerical index of podzol and podzolic soil development. Physical Geography 9, 232–246.

Soil Survey Division Staff, 1993. Soil Survey Manual. USDA Handbook, vol. 18. US Government Printing Office, Washington, DC. 437 pp.

Soil Survey Laboratory Staff, 1996. Soil survey laboratory methods manual. USDA-SCS, National Soil Survey Center. Soil Survey Investigations Report. 42, Version 3.0. National Soil Survey Center, Lincoln, NE.

Soller, D.R., Owens, J.P., 1991. The use of mineralogic techniques as relative age indicators for weathering profiles on the Atlantic Coastal Plain, USA. Geoderma 51, 111–131.

Ugolini, F.C., Minden, R., Dawson, H., Zachara, J., 1977. An example of soil processes in the Abies amabilis zone of central Cascades, Washington. Soil Science 124, 291–302.

Van der Plas, L., Tobi, A.C., 1965. A chart for judging the reliability of point counting results. American Journal of Science 263, 87–90.

Velbel, M.A., 1987. Rate-controlling factors in the weathering of some ferromagnesian silicate minerals. Transactions, 13th Congress of the International Society of Soil Science, Hamburg, Germany, vol. 6. pp. 1107–1118.

Velbel, M.A., 1989. Weathering of hornblende to ferruginous products by a dissolution–reprecipitation mechanism: Petrography and stoichiometry. Clays and Clay Minerals 37, 515–524.

Velbel, M.A., 1993. Formation of protective surface layers during silicate–mineral weathering under well-leached, oxidizing conditions. American Mineralogist 78, 405–414.

White, A.F., Brantley, S.L. (Eds.), Reviews in Mineralogy, Chemical Weathering Rates of Silicate Minerals, vol. 31. Mineralogical Society of America, Washington, DC. 583 pp.