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HORNBLENDE ETCHING AS AN INDICATOR OF SOIL DEVELOPMENT AND RELATIVE WEATHERING AMONG SPODOSOLS

By

Leslie Renee Mikesell

A THESIS

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

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ABSTRACT

HORNBLENDE ETCHING AS AN INDICATOR OF SOIL DEVELOPMENT AND RELATIVE WEATHERING AMONG SPODOSOLS

By

Leslie Renee Mikesell

Hornblende etching holds great promise as a relative weathering indicator and as another soil development indicator. This research was designed to test hornblende denticulation amplitude as a weathering indicator, by comparing it to a standard weathering indicator (quartz/feldspar ratios), and to determine its reliability as an indicator of soil development by comparing it to four soils in various stages of development. The natural weathering of hornblende produces etching, which results in a "denticulated" margin. These features gradually and systematically increase in depth and size. In this study, hornblende denticulation amplitude measurements exhibited a clear trend showing more extensively weathered grains up profile, and therefore should be considered an indicator of weathering. Hornblende denticulation amplitude is a record of weathering, which perhaps more accurately reflects weathering intensity rather than duration. The denticulation amplitude measurements also mimicked the soil development order of the four soils showing that it will also serve as a relative weathering indicator among soils of the same age. Due to the fact that it correlated with the rank order of soil development, it can also be used as a soil development indicator. In this study, mineral weathering appears to be related to the degree of soil development in soils representing different degrees of development but of the same age.

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"Can you fathom the mysteries of God? ...speak to the earth, and it will teach you, ...for does it not know that the hand of the Lord has done this?" Selections from Job 11 and 12.

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KEY TO SYMBOLS OR ABBREVIATIONS

μmmicrometer

- AAO.....acidified ammonium-oxalate
- AAS.....atomic absorption spectrometer
- CD.....sodium citrate-dithionite
- EDS.....energy-dispersive spectrograph
- Fe_d and Al_diron and aluminum extracted with sodium citrate-dithionite
- Fe_o and Al_o....iron and aluminum extracted with acidified ammonium-oxalate
- Fe_p and Al_p.....iron and aluminum extracted with sodium pyrophosphate
- PP.....sodium pyrophosphate
- SEMscanning electron micrograph
- vs.....versus
- yr B.P.years before present

INTRODUCTION

Hornblende Etching as a Relative Age Indicator

Hornblende etching holds great promise as a relative weathering indicator. Hornblende, a member of the amphibole class of minerals, is common and abundant on the earth's surface (Blackburn and Dennen, 1988). Natural weathering of hornblende corrodes the hornblende in a crystallographically controlled manner, resulting in etch pits on the surface of the mineral and a "sawtooth" or "denticulated" margin on which the "teeth" are parallel to the c-axis (e.g., Berner et al., 1980; Berner and Schott, 1982; Velbel, 1987, 1989) (Figure 1). Progressive weathering causes these features to gradually and systematically increase in depth and size from a well-defined starting point (Locke, 1979, 1986; Birkeland, 1978), the Antarctic (Ugolini and Bull, 1965; Everett, 1971; Locke, 1979, 1986). Using this knowledge, hornblende etching has been applied



Figure 1. Scanning electron micrograph showing naturally weathered homblende with etch pits, denticulated margin, and "teeth" parallel to the c-axis. Arrow indicates c-axis direction. Image taken at the Center for Advanced Microscopy at Michigan State University by Leslie Mikesell and Ewa Danielewicz. as a relative age indicator of soils in the Rocky Mountains of the United States (Hall and Heiny, 1983; Hall and Martin, 1986; Hall and Michaud, 1988), the Canadian Arctic (Everett, 1971), and Italy (Andrews and Miller, 1980). This was accomplished by statistically comparing the depth of hornblende denticulation, or denticulation amplitude, in soils and sediments of different ages (Locke, 1979). Hornblende from the older sites exhibited a greater degree of etching, as measured by greater amplitude, than the hornblende from the younger sites (Locke, 1979). Thus, it was concluded that hornblende could be used to determine relative age.

In the previously mentioned studies, the researchers assumed that time of exposure, or duration of weathering, was the primary factor that influenced denticulation amplitude. These studies were based on the idea that etch features enlarge over time without taking into consideration other factors that may affect this enlargement. Factors, other than time, that may significantly contribute to this weathering process include: climate, amount of water present, pH of soil, presence and abundance of clay, and presence of organic matter (White and Brantley, 1995). Previous work has only emphasized the relationship between hornblende denticulation and the duration of weathering. However, hornblende denticulation amplitude is a cumulative record of weathering, which reflects both the weathering intensity and the weathering duration. Thus, denticulation amplitude measurements might serve as a relative weathering indicator among soils of the same age but differing degrees of development.

Quartz/Feldspar Weathering Ratio

The quartz/feldspar ratio is a measure used to determine the degree of mineral

weathering based on the persistence of quartz compared to that of feldspar (e.g., Birkeland, 1974; Muhs 1982; Bockheim et al., 1996). From Goldich's (1938) study, we know that a sediment will become depleted in feldspar with respect to quartz as weathering continues because feldspar is less persistent than quartz. Since the hornblende denticulation amplitude may also indicate the degree of mineral weathering, these two measurements can provide information regarding the degree of mineral weathering.

Soil Development

Many researchers have assumed that mineral weathering and soil development occur simultaneously. Due to this assumption, or poor word choice, the terms "weathering" and "soil development" have often been used interchangeably in the literature (e.g., Ruhe, 1956; Locke, 1979; Andrews and Miller, 1980). However, weathering and soil development are two different but inter-related processes (e.g., Fanning and Fanning, 1989). Weathering is the alteration of rock and minerals, at or near the Earth's surface, due to environmental conditions (Bland and Rolls, 1998). On the other hand, soil development is the amount of pedologic change, including horizonation, that has taken place in a parent material (Birkeland, 1999) and is a function of climate, biota, topography, parent material, and time (Jenny, 1941). It is possible that soil development and weathering will correspond to each other, and that a measure of one may proxy for a measure of the other, but the two measures are not necessarily providing the same information about the soil. If hornblende denticulation amplitude can produce the same trend with regards to relative weathering as soil development does with regards

to relative profile development, hornblende denticulation amplitude could be used as a proxy for soil development.

Research Questions

Soil development is a function of several factors; these include climate, biota, topography, parent material, and time (Jenny, 1941). The influence of any one factor is studied by examining a sequence of soils in which all but one of these soil-forming factors are held as constant as possible, so that only one factor varies in the sequence (Birkeland, 1999). Using this approach, the degree of hornblende weathering, as measured by denticulation amplitude, has been used to determine relative age of soils on glacial parent materials in studies where time or soil age is the only soil-forming factor allowed to vary (e.g., Hall and Heiny, 1983; Locke, 1979, 1986; Birkeland, 1978). However, the influence of soil-forming factors other than time on hornblende weathering remains to be examined. As Fanning and Fanning (1989) point out, soil-development involves a variety of processes, of which weathering is only one, and some aspects of soil development can proceed without progress in mineral weathering, and vice versa. Thus, a number of questions relating hornblende weathering to soil development remain. These include: 1) is hornblende weathering (as one type of mineral weathering) related to or independent of soil development? and 2) is hornblende denticulation amplitude comparable to other measures of mineral weathering?

Purpose of Study

This research was designed to examine the relationship between mineral

weathering in general, hornblende weathering in particular, and soil development. In order to examine these relationships, four soils, similar in age but at various stages of development, from northern lower Michigan were sampled for this study. Denticulation amplitude measurements were taken from each horizon in every pedon. A plot of horizon vs. denticulation amplitude was then constructed to determine if any correlations could be made. A quartz/feldspar ratio was also determined for each horizon, and a horizon vs. quartz/feldspar ratio plot was then constructed and examined to determine if correlations could be drawn from these plots. If it is determined that correlations may be drawn between hornblende denticulation amplitude, or quartz/feldspar ratios, and soil development, it would provide researchers with other analytical tools that might be useful in situations where traditional analysis do not yield conclusive results.

CHAPTER 2

Hornblende Weathering

General Description of Hornblende

Hornblende is the most common mineral species of the amphibole group. It is a ferromagnesian mineral in the inosilicate mineral class (Blackburn and Dennen, 1988), having the general composition of

[$(Na,K)_{0-1}Ca_2(Mg,Fe^{2+},Fe^{3+},Al)_5Si_{6-7.5}Al_{0.5-2}O_{22}(OH)_2$] (Brantley and Chen, 1995). Inosilicates are characterized by silica tetrahedra that are linked in double chains by sharing alternately two and three oxygen atoms per tetrahedron (Brantley and Chen, 1995).

Blackburn and Dennen (1988) describe hornblende as black to dark green, and it generally appears columnar, bladed, or fibrous, but can also be granular massive. The crystallography of hornblende is monoclinic, 2/m. Its crystals are perfect prismatic {110} at 56° and 124°, with good cleavage also at 56° and 124°. Hornblende has subconchoidal to uneven fracture, with a hardness of 5 - 6, and a specific gravity of 2.9 - 3.3.

Hornblende Distribution

Hornblende is widely distributed in igneous rocks and is often associated with quartz, feldspar, and pyroxene. It is also a common component of metamorphosed basaltic rocks (Blackburn and Dennen, 1988). Goldich (1938) found hornblende to be more persistent than olivine, pyroxene, or calcic plagioclase during weathering, but less persistent than micas, alkali feldspars, or quartz. Because it is common in both igneous

and metamorphic rocks, it is abundant in transported material as well. Several studies have found that it is the most abundant of the heavy minerals in soils formed in a variety of parent materials, including hornblende schist in central Texas (Stahnke, 1965, as cited in Allen and Hajek, 1989), loess-mantled till in southwestern Iowa (Ruhe, 1956), glacial till in southwestern Montana (Hall and Martin, 1986), glacial till in Ontario, Canada (Dreimanis et al., 1957), glacial till in the northeastern United States (Johnson and Chu, 1983, as cited in Allen and Hajek, 1989), soils in the Great Lakes region (Dworkin et al., 1985), glacial till in south-central Michigan (Haile-Mariam and Mokma, 1996), and sandy outwash material of northern Michigan (Haile-Mariam and Mokma, 1995). Because hornblende is common and widespread, better understanding of its weathering is potentially widely applicable.

Weathering Environment

Soil environments that are well drained and leached are more conducive to weathering than environments that are poorly drained (Cremeens et al., 1992; Haile-Mariam and Mokma, 1996,1995). Berner (1978) found that flushing water through rock, sediment, or soil removed dissolved weathering products so that they are no longer in contact with the mineral, thus increasing the dissolution rate. He went on to state that with continuous flushing, a limit could be reached where the flushing rate is no longer a controlling factor, but the mineral reactivity controls the rate. This occurs when sufficient water passes through the rock or soil to remove any weathering product, at which point the factor that controls the dissolution rate is the reactivity of the mineral. In the unsaturated zone of a soil, flushing controls the dissolution rate due to an insufficient

amount of water. Therefore, the most influential climatic factors on hornblende etching are effective precipitation and infiltration of unfrozen water (Locke, 1979).

Hornblende Weathering Rates

Weathering rates have been determined for naturally weathered hornblende by studying the mean maximum etching depth, or MMED, (Locke, 1979, 1986) and etch pit distribution (Cremeens et al., 1992; MacInnis and Brantley, 1993). These rates were generally found to be $10^1 - 10^4$ times slower than the experimentally determined rates (MacInnis and Brantley, 1993; White et al., 1996). The general discrepancy between natural weathering rates, and experimentally determined rates, is discussed in detail by Velbel (1993a). Brantley et al. (1993) provide possible explanations for the difference between weathering rates determined in the laboratory and those determined by naturally weathered hornblende, such as: lack of understanding of reaction mechanisms, experimental error, inaccuracies in reactive surface area estimation, inaccuracies in wetted surface area estimation, temperature variability, and biological processes. Another possible reason for the discrepancy in these rates is the changing dissolution rates in the natural environment due to rate constants that decrease with time (White et al., 1996; Hall and Martin, 1986). Murakami et al. (1998) also found a discrepancy between natural rates and laboratory determined rates of weathering in anorthite due to the decreasing weathering rate in nature. However, they concluded that these rates decreased due to the saturation effect caused by secondary minerals between grains. Not only are weathering rates slower in nature relative to laboratory experiments, but they also differ between the upper part of the profile where the rate is rapid, and the lower part

of the profile where the rate is slow (Markos, 1975).

Several possible factors that could affect the dissolution rate of minerals in the natural environment include: precipitation of dissolved silica, iron precipitates, and organic and inorganic coatings on grain surfaces (Dove, 1995). Nugent et al. (1998) found thin, hydrous, patchy natural coatings of amorphous and crystalline aluminosilicate on feldspar grains that were only visible under atomic force microscopy. They concluded that these coatings were partially inhibiting dissolution and thus contributing to the discrepancy between natural and laboratory determined weathering rates. However, Velbel (1993b) argued that examination of naturally weathered silicate minerals reveals etch pits, which are features produced when chemical reactions at the interface control the weathering rate. The presence of etch pits on surfaces beneath clay coatings or oxide and/or hydroxide products indicate diffusion through a surface layer is not rate-limiting. Similarly, Berner and Schott (1982) found that cation-depleted layers on soil grains were too thin to be considered diffusion-limiting, and therefore weathering is controlled by surface chemistry and not by diffusion through a surface layer. However, precipitates and alteration products could slow dissolution rates by blocking or altering flow paths, and thus decrease the amount of water that reaches the mineral (Eggleton, 1986, as cited by Brantley and Chen, 1995; Velbel, 1993b; Murakami et al., 1998).

Hornblende Weathering Features

Natural weathering of hornblende forms etch pits on the surface of the grain. These dissolution voids may be seen using a petrographic microscope. Velbel (1989) noted that hornblende weathering progresses through a sequence of features that indicate

the extent of weathering. The earliest feature of weathering (under oxidizing conditions) is the presence of ferruginous material along grain boundaries or in fractures within the grain observed in thin section. This chemical precipitation of goethite, gibbsite, or kaolinite produces a boxwork structure. The more extensively weathered hornblende exhibits crystallographically controlled etch pits, which form parallel to the c-axis in the direction of cleavage (Figure 2). This feature is formed by the selective weathering at crystal defects and dislocations (Berner et al., 1980; Velbel, 1993b). More advanced weathering produces a sharp denticulated margin, also known as cockscomb termination, hacksaw termination (e.g., Berner et al., 1980; Berner and Schott, 1982; Velbel, 1987, 1989, 1993b), or "sawtooth" termination (Velbel, 1989) (Figure 3). These denticulations result from side-by-side coalescence of lenticular, or lens-shaped, etch pits (Berner et al., 1980; Berner and Schott, 1982; Velbel, 1993b). Velbel (1989) goes on to state that even more advanced weathering produces hornblende remnants that occupy dissolution cavities bounded by ferruginous boxworks (Figure 4). These are void spaces that lack weathering product, either in the cavity or on the hornblende surface. If the parent hornblende is removed through dissolution, a "negative pseudomorph" or alveoporomorph (terminology of Delvigne, 1998) is left (Figures 5 and 6). An interesting feature of hornblende weathering observed by Velbel (1989) was pendants of ferruginous material that were separated from the hornblende remnants by void space (Figure 4). This separation suggests that the pendants formed by dissolution-reprecipitation, or neoformation.

Hornblende etch pits progress through a sequence of stages (Berner et al., 1980; Berner and Schott, 1982; Cremeens et al., 1992). These stages begin with the formation

of one or more lens-shaped etch pits that enlarge with weathering (Figure 7). The etch pits then coalesce either end-to-end or side-by-side. End-to-end coalescence results in the formation of longitudinal grooves or striations (Figure 8). It is the side-by-side coalescence of etch pits that form the denticulated margin (Figure 3). These tooth-like denticulations are unweathered hornblende, which are adjacent to pits that formed by the dissolution of the hornblende.

Etch pits are crystallographically controlled dissolution voids, produced by interface-limited weathering mechanisms (Velbel, 1993b, and references contained therein). Berner and Schott (1982) put forth the idea that this mechanism consists of H⁺ attacking the mineral at a point of excess energy, primarily at a dislocation outcrop, which is accompanied by Fe oxidation in the outermost atomic layers. This selective attack also occurs at crystal defects (Berner et al., 1980). However, this does not penetrate inward over time, but produces lens-shaped etch pits (Berner and Schott, 1982).



Figure 2. Scanning electron micrograph of crystallographically controlled etch pits, which form parallel to the c-axis in the direction of cleavage. Arrow indicates c-axis direction. Image taken at the Center for Advanced Microscopy at Michigan State University by Leslie Mikesell and Ewa Danielewicz.



Figure 3. Petrographic micrograph of "sawtooth" termination on a naturally weathered hornblende grain. Image captured with a Pixera digital imaging system.



Figure 4. Scanning electron micrograph of weathered homblende showing ferruginous microboxwork (B) separated from denticulated homblende (D) by void space with pendants (P) projecting from the microboxwork into the void space (Figure 6 in Velbel, 1989).



Figure 5. Photomicrograph showing hornblende has been completely removed, leaving only ferruginous boxwork (B) and pendants (P), or "negative pseudomorph" (Figure 9 in Velbel, 1989).



Figure 6. Scanning electron micrograph showing ferruginous boxwork (B) with neoformation pendants (P) (Figure 8 in Velbel, 1989).



Figure 7. Scanning electron micrograph of enlarged lens-shaped etch pits in naturally weathered homblende. Image taken at the Center for Advanced Microscopy at Michigan State University by Leslie Mikesell and Ewa Danielewicz.



Figure 8. Scanning electron micrograph of end-to-end coalescence of etch pits forming grooves or striations in naturally weathered hornblende (Figure 3 in Velbel, 1989).

Cremeens et al. (1992) suggested that etch pits uniform in size and shape might be associated with strain due to exsolution lamellae. They also concluded irregularly shaped and spaced pits might be associated with microcracks and fractures.

Hornblende Weathering in Soils

The weathering of hornblende can produce different weathering features and products depending on environmental conditions. Etch pit size and shape could be an indicator of the environment in which they formed. Cremeens et al. (1992) studied the etch pits in orthoclase and pyriboles. They observed that in poorly drained soils the minerals had small pits but a large number of them. This suggested a slower growth rate and presumably less flushing with fresh water. Greater coalescence of pits was observed in well drained soils. These pits were larger, irregularly shaped, and elongated, suggesting a greater growth rate, which they attributed to increased flushing of fresh water, which would remove the weathering products and reduce contact time of the primary mineral with its weathering products.

In a study conducted in Maryland, the weathering products of hornblende, such as Fe oxides and oxyhydroxides and clay minerals, were dependant upon the intensity of leaching in the profile (Cleaves, 1974). Cleaves (1974) also found that in a poorly drained, structured saprolite developed on a quartz-plagioclase-hornblende gneiss, hornblende weathered to montmorillonite. It weathered to ferric oxides in a well drained, structured saprolite developed on the same quartz-plagioclase-hornblende gneiss parent material. He also noted that the weathering products of hornblende in a well drained saprolite (which developed on an epidote amphibolite) included kaolinite, halloysite,

goethite and other ferric oxides, and isotropic amorphous material. Velbel (1989) found that hornblende weathered to goethite, gibbsite, and kaolinite in an intensely leached weathering profile on a plagioclase-hornblende gneiss of the Carroll Knob mafic complex of North Carolina. Other weathering products of hornblende include: iron-rich montmorillonite (Walker et al., 1967), vermiculite, chlorite (Stephen, 1952, as cited by Huang, 1989), beidellite (Goldich, 1938), and smectite (Rice et al., 1985).

In the soil, hornblende is most commonly found in the sand and silt size fraction where it constitutes a significant portion of the heavy minerals (Ruhe et al., 1966; Locke, 1979; Allen and Hajek, 1989). Haile-Mariam and Mokma (1995, 1996) studied the mineralogy of two fine-loamy hydrosequences in south-central Michigan, and two sandy Spodosol hydrosequences also in Michigan. In all the pedons studied, they found that the percent of hornblende increased with depth, as the percent of quartz decreased with depth. They attributed this trend to the persistence of quartz compared to other minerals.

In addition to mineral depletion trends, hornblende etching trends have been observed in soils. Locke (1979) conducted a study on the etching of fine sand sized hornblende collected from a coarse-grained glacial deposit from Baffin Island, Canada. He found that etching decreased logarithmically with increasing depth in the profile. He also noted that the rate of etching at any give depth decreased logarithmically with increasing soil age. He proposed that precipitation and unfrozen water infiltration influenced the etching rate as a function of depth and age. Based on these observations, Locke (1979) felt that hornblende etching showed great promise as a relative dating technique.
In a later study, Locke (1986), found that soils of similar age exhibit trends where hornblende etching was greatest near the surface and decreased with depth. This trend was interpreted to be due to a decrease in soil wetting events at depth. He also noted that hornblende etching showed significant differences in soils of similar age that formed under different climatic regimes. This difference in hornblende etching was attributed to differential rainfall. This precipitation theory was supported by Hall and Horn (1993), who studied soils of two chronosequences, one each from the Wind River Range in western Wyoming and the Tobacco Root Range in southwestern Montana, U.S.A. They found faster weathering rates in the soils at higher elevations due to increased orographic precipitation.

CHAPTER 3

Quartz and Feldspar Weathering

Mineral Persistence

Many studies have been conducted to determine the stability of minerals by comparing the mineral composition of the fresh parent material to its weathering product (e.g., Goldich, 1938; White et al., 1996; Birkeland, 1999). This comparison allowed researchers to quantify the relative depletion of a mineral from a system. Less stable minerals are preferentially depleted. Using relative depletion data, weathering sequences have been developed that rank minerals according to their stability (Goldich, 1938; Pettijohn, 1941, as cited in Bland and Rolls, 1998; Ollier and Pain, 1996).

Samuel Goldich (1938) developed the weathering sequence that is still the standard today. Goldich (1938) developed what he called a mineral-stability series in weathering by conducting extensive analyses on fresh and weathered materials from several sites. He studied a fresh amphibolite from the Black Hills of South Dakota and found it to be 77 percent hornblende while its residual material was only 7 percent hornblende. He concluded that hornblende was undergoing extensive alteration to beidellite or related clay minerals.

Goldich (1938) also studied the Morton Gneiss in Minnesota. He concluded that the heavy minerals of this granite gneiss had been largely destroyed and that the remaining minerals represented the relatively resistant or more stable minerals. The least stable minerals were plagioclase, hornblende, epidote, titanite, and apatite, whereas ilmenite-magnetite, biotite, microcline, and orthoclase were more resistant. Quartz and

zircon were the most stable minerals, with even these showing signs of being altered.

Additionally, Goldich (1938) analyzed the Medford diabase from eastern Massachusetts. He found an absolute loss of heavy minerals as a result of weathering. He also noted the relative abundances of heavy minerals in the fresh and weathered diabase suggested that the rate of weathering differed for various minerals. From this diabase, Goldich ranked the minerals from least to most stable: chlorite, pyroxene, epidote, hornblende, biotite, apatite, and magnetite-ilmenite.

From this classic study, Goldich (1938) proposed a mineral-stability series for weathering in which the minerals were ranked from least stable to most stable as: olivine, augite, hornblende, biotite, potassium feldspar, muscovite, and quartz (Figure 9). The plagioclase series is separate from the mafic series with sodic plagioclase being more stable than calcic plagioclase. As a group, the mafic minerals are less stable than felsic minerals.

MINERAL-STABIL	ITY SERIES IN WEATHERING
Olivine	
	Calcic plagioclase
Augite	
	Calcic-alkalic plagioclase
Hornblende	Alkali-calcic plagioclase
	Alkalic plagioclase
Biotite	
	Potash feldspar
	Muscovite
	Quartz
	-



Despite its historical precedence, Velbel (1999) points out that the term "stability series" is a misnomer. The series proposed by Goldich (1938) and the many that followed (e.g., Pettijohn, 1941, as cited in Bland and Rolls, 1998; Dryden and Dryden, 1946; Nickel, 1973; Morton, 1984; Bateman and Catt, 1985; Allen and Hajek, 1989; White et al., 1996; Velbel, 1999) rank the persistence of different minerals. These rankings are due to the kinetics of the reactions, not the thermodynamic stability of the mineral. A more accurate term for these series should be "mineral persistence series".

Quartz and Feldspar

Two relatively abundant minerals that are commonly compared, and which were chosen for this study, are quartz and feldspar. A soil will become depleted in feldspar, with respect to quartz, because feldspar is less resistant to weathering than quartz (e.g., Goldich, 1938; Ollier and Pain, 1996; Birkeland, 1999).

Quartz, with the formula of SiO₂, is a member of the silica group of tectosilicates. The basic building block of silicate minerals is the tetrahedron, where a Si⁴⁺ is surrounded by four O²⁻ ions. The tectosilicates are those silicate minerals in which all oxygens are shared with adjacent tetrahedra to form a network with the net charge of zero (Blackburn and Dennen, 1988). Blackburn and Dennen (1988) provide a summary of crystallography, physical properties, and occurrence of quartz. Quartz forms hexagonal prisms with pyramidal termination and can have either left- or right-handed forms. It is usually found massive or as crystals. Quartz has no cleavage and no parting. It has irregular to conchoidal fracture. Quartz has a hardness of 7 and a specific gravity of 2.65. Quartz is one of the most abundant minerals and is an important constituent in many

igneous, metamorphic, and sedimentary rocks. It is a major component in some rocks, such as sandstone and quartzite. Quartz is often the sole constituent in veins and is almost universally found in soils and sediments. Ollier and Pain (1996) note that quartz is often the last mineral to crystallize from a magma, and due to this lower temperature of crystallization, it is fairly stable at earth surface temperatures. Although quartz is extremely resistant to chemical weathering, physical weathering by wind or water can round quartz grains. Due to its resistance to chemical weathering, quartz can be a standard by which the weathering of other grains can be measured. Ollier and Pain (1996) state that due to its persistence, the proportion of quartz increases up profile because as other minerals are removed higher in the profile, quartz remains.

Feldspars are aluminosilicate minerals, with the alkali feldspars having the general formula (K,Na)(AlSi₃O₈) and the plagioclase feldspars having the general formula (Na,Ca)(Al,Si)₄O₈ (Blackburn and Dennen, 1988). Blackburn and Dennen (1988) provide a summary of the feldspars. The distinction between the alkali feldspars and the plagioclase feldspars is not always clear-cut due to solid solution. However, the alkali feldspars are monoclinic, or, if triclinic, have more K than Ca. The plagioclase feldspars are triclinic with less K than Na or Ca. Due to the solid solution, a wide range of chemical composition is permissible. Twinning is very common among the feldspars, occurring as simple or repeated twins. The feldspars make up almost 60% of igneous and metamorphic rocks, which constitute over 90% of the earth's crust. Feldspars are found in the light fraction of soils and have a specific gravity of 2.6. Ollier and Pain (1996) note that feldspars alter rapidly due to the pronounced cleavage that probably allows rapid penetration of water. Feldspars often alter to kaolin, but other secondary minerals,

such as mica and allophane, can also be formed.

Quartz/Feldspar Ratio

Quartz/feldspar ratios examine the relationship between a resistant mineral and a non-resistant mineral. In the soil environment, feldspar is more quickly leached than quartz (Nesbitt et al., 1997). Nesbitt et al. (1997) describe this relationship in a simplified model that has plagioclase and K-feldspar leached at approximately the same rate, which is 100 times faster than quartz. When dissolution begins, the soil quickly reaches silica saturation with respect to quartz. This saturation limit causes quartz to stop dissolving, however feldspar and plagioclase continue dissolving. Generally, silica saturation with respect to K-feldspar is reached next allowing only plagioclase to continue dissolving. They also note that the soil environment is critical in these reactions because the amount of organic acids present determines the amount of mineral dissolution.

Studies have shown that the feldspar content of a soil decreases in the upper horizons due to an increasing of weathering intensity (e.g., Nesbitt et al., 1997; Allen and Hajek, 1989). Birkeland (1974) stated that this observation is one way of determining weathering rates. Rate determination is accomplished by establishing the ratio of a resistant mineral (e.g. quartz) to a nonresistant mineral (e.g. feldspar) in the parent material and comparing that to the ratio of the same minerals in a horizon of known age. This gives the rate at which the less resistant mineral is depleted. This is the technique Ruhe (1956) used in Iowa when estimating that the Wisconsin surface had weathered 6800 years, the soil of the late-Sangamon surface at least 13,000 years, and the soil related to the Yarmouth-Sangamon surface 10⁵ years or more.

Relative age may also be determined by using quartz/feldspar ratios (Dorronsoro and Alonso, 1994). Dorronsoro and Alonso (1994) concluded soils of different ages would have different quartz/feldspar ratios under conditions that hold other soil forming factors constant. The soil with the larger ratios, indicating more depletion of feldspar, is the older soil, thus providing relative age.

Quartz/feldspar ratios also serve as a relative weathering indicator (Ruhe, 1956; Nesbitt and Markovics, 1997). Ruhe (1956) noted that a comparison of the weathering ratios for each site in his study indicated the intensity of weathering was greatest in the older surface. The older surface had ratios with higher values, which suggested there were greater amounts of resistant minerals relative to less resistant minerals. These conclusions indicate the quartz/feldspar ratio could be used as a relative weathering indicator.

Quartz/feldspar ratios have also been used to determine parent material uniformity due to the stability of quartz and abundance of both quartz and feldspar (Wilding et al., 1977; Osei, 1992).

Lithological discontinuities can be detected using quartz/feldspar ratios (Price et al., 1975; Osei, 1992). Price et al. (1975) were able to distinguish the boundary between an overlying loess and the underlying residuum by constructing a depth vs. quartz/feldspar ratio plot for three profiles in their research area. They noted there was a fairly uniform quartz/feldspar ratio to a depth of about 100cm at which point there was a large increase in the ratio. They concluded this large increase indicated a lithological discontinuity.

CHAPTER 4

Spodosols

Podzolization

Podzolization is the pedogenic process by which Fe, Al, and organic carbon are translocated down the soil profile from the O, A and E horizons to an illuvial horizon. The driving force behind this process is the percolation of acidic water through the soil profile. Infiltrating water becomes acidic as it passes through the decaying leaf litter of the O horizon. This process produces Podzol or Spodosol profiles (DeConinck, 1980; Buurman and van Reeuwijk, 1984; Schaetzl and Isard, 1991; Mokma and Evans, 2000; Schaetzl, 2002).

The podzolization process can be summarized in the following four steps: (1) organic material on the surface decays and fulvic acids are produced which are carried by the water as it percolates through the profile, (2) organic matter then complexes with and mobilizes Fe^{3+} and Al^{3+} cations, (3) these mobile cations are translocated from the O, A and E horizons to the B horizon where (4) the Fe and Al are deposited (Mokma and Evans, 2000).

The fulvic acids, percolating through the soil with the water, acidify the upper horizons. This acidic environment causes intense weathering of the minerals, which release cations; of particular interest are Fe and Al. The Fe and Al are then translocated down the profile (Mokma and Evans, 2000). There are two current theories to explain the translocation of Fe and Al during podzolization. One theory states that the fulvic acids chelate the Fe and Al to form organometallic complexes that are then translocated

in percolating water. Once the complexes reach the water table, or a less permeable layer, microbes break down the fulvic acid thus causing the precipitation of the Fe and Al (DeConinck, 1980; Buurman and van Reeuwijk, 1984). The other theory is the "protoimogolite" theory. This theory was developed by researchers who observed that Fe and Al exist in amorphous, inorganic compounds such as imogolite and allophane. According to this view, the Fe and Al are translocated into the B horizon as protoimogolite first, and then organic matter precipitates onto the Fe and Al (Farmer et al., 1980; Farmer, 1982; Anderson et al., 1982). Some aspect of each theory, and possibly a combination of the two, might better explain the translocation of Fe and Al during podzolization rather than either theory independently (Wang et al., 1986; Jakobsen, 1991; Schaetzl, 2002).

Factors Contributing to Podzolization

Several factors contribute to the rate of podzolization. These factors include: (1) climate, especially snowmelt infiltration, (2) parent material texture, (3) parent material composition, and (4) type of vegetation in the region.

Climate affects the rate of podzolization by determining not only the amount of precipitation, but just as importantly, it determines whether or not that precipitation infiltrates. Schaetzl and Isard (1996) observed that regions that received little snow during the winter had a slower rate of podzolization than regions that received enough snow to accumulate a deep winter-long snowpack. The soil under deep snowpack is insulated and does not freeze often, unlike soil that has little snow accumulation (Isard and Schaetzl, 1998). The insulated soil is impacted by a high amount of infiltration of the

snowmelt during spring, due to the quantity of meltwater available and the permeability of the non-frozen soil. The frozen soil does not allow for infiltration during spring until it has thawed, by which time there may be little or no snowmelt remaining to enter the profile (Schaetzl and Isard, 1996). Because long, continuous influxes of meltwater contribute to the rate of podzolization, climate is an important factor.

Parent material texture is a significant control on podzolization. The best expressed Spodosol profiles are in coarse-textured soils (Gardner and Whiteside, 1952; Messenger et al., 1972; Vance et al., 1986; Schaetzl and Isard, 1991). The coarse texture results in more rapid permeability and higher infiltration rate of the acidic water. Podzolization is inhibited by high clay contents. Mokma and Evans (2000) stated that clay might slow or even stop the translocation of Fe and Al by adsorbing the Fe and Al cations, thus making them immobile. Due to this, the E and B horizons will not thicken quickly and the B horizons will redden slowly. Another way clay interrupts the process is by weathering so quickly in the acidic water that it releases more cations than the system can handle. The few chelating acid molecules get overwhelmed and immobilized, stopping the translocation. For these reasons, clay in the soil parent material must be minimal or weathered extensively by acidic water prior to podzolization.

In the best expressed Spodosols, the parent material is sandy and composed primarily of quartz with lesser amounts orthoclase, plagioclase, pyroxene, amphibole, mica, and opaque minerals (Haile-Mariam and Mokma, 1995; Mokma and Evans, 2000). Carbonate minerals are notably few in the parent material. Any carbonate minerals present will react with the percolating water to neutralize the acid and slow the rate of podzolization (Mokma and Evans, 2000). Therefore, most of the carbonates must be

weathered and leached from the system for podzolization to progress.

Vegetation also contributes to the rate of podzolization. Schaetzl (2002) noted that certain types of coniferous vegetation, such as pine and hemlock, accelerate podzolization. The leaf-litter under conifers is composed of needles, which are more acid than the leaf-litter under broadleaf trees. Decay of the conifer needles produces more of the acids needed for podzolization. For this reason, Spodosols are associated with coniferous and coniferous-deciduous forests.

The Spodosol Profile

Spodosols have four major horizons (Mokma and Evans, 2000). The O and/or A horizon is dark brown to black due to the high organic content. The process of podzolization leaves a gray to ashy white eluvial zone, or E horizon, from which Fe and Al have been removed. The E horizon is below the A horizon and above the B horizon, which is a dark reddish brown illuvial zone where the Fe and Al have accumulated. The illuvial zone is a spodic (Bs or Bhs) horizon. There may be several B subhorizons; those directly below the E horizon are usually reddest and darkest becoming more yellow down profile. The underlying C horizon usually has an even more yellow hue than the lowest B horizon.

As a Spodosol develops, the E horizon becomes whiter while the Bs or Bhs horizon continues to darken and thicken. The POD index is a numerical index of Spodosol development based on this pathway of development (Schaetzl and Mokma, 1988). This number is calculated using the differences of Munsell hues between the eluvial and illuvial horizons. Due to the requirement of an eluvial horizon being present

in the soil, a POD index cannot be calculated for a pedon lacking an E horizon. If both eluvial and illuvial horizons are present, redder hues in the B horizons, and more B subhorizons, will result in a higher POD index. A higher number indicates a more strongly developed Spodosol.

Extractable Iron and Aluminum in Spodosols

Iron and aluminum exist in soils in various pedogenic forms. When identifying a spodic horizon, the Fe and Al content must be determined because the horizon is characterized by the accumulation of translocated Fe and Al (McKeague and Day, 1965; Soil Survey Staff, 1999). Three extractants are commonly used in this determination. Sodium citrate-dithionite (CD) is used because it primarily extracts "free" Fe, denoted by Fe_d , from pedogenic iron oxides, and "free" Al, denoted by Al_d , from aluminum oxides (Birkeland, 1999; Weisenborn, 2001). The term "free" is used to describe compounds having a single species of coordinating cation (Jackson et al., 1986; Weisenborn, 2001). The term is also used for an iron oxide that can be reduced and dissolved by a dithionite treatment (Anonymous, 1996; Weisenborn, 2001). Acidified ammonium-oxalate (AAO) extracts "active" Fe, denoted by Fe₀, and "active" Al, denoted by Al₀, 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; Weisenborn, 2001). AAO also extracts Al from noncrystalline, or amorphous, aluminosilicates such as allophane and imogolite and other weathering products (Farmer et al., 1983). Fe₀ selects Fe mainly from ferrihydrite (Fe₅HO₈•4H₂O), and is such a good test that its value may be multiplied by 1.7 to estimate the amount of ferrihydrite present (Parfitt and

Childs, 1988; Birkeland, 1999). The third extractant is sodium pyrophosphate (PP). It extracts Fe, denoted by Fe_p , and Al, denoted by Al_p , from organically-bound complexes and, to a lesser degree, noncrystalline hydrous oxides. It has been reported and long assumed that these three extractants do not extract Fe and Al from crystalline minerals (Mehra and Jackson, 1960; Ross and Wang, 1993; McKeague et al., 1971).

In addition to analyzing the extraction data directly, various calculations and formulations may be made from the raw data. These calculations indicate the form of Fe and Al that is found in each horizon (e.g., crystalline or noncrystalline, complexed or not). The ratio of AAO / CD, or "activity ratio" (Blume and Schwertmann, 1969), measures the amount of pedogenic Fe that is amorphous, plus ferrihydrite (Birkeland, 1999). It approximates the relative crystallinity of "free" oxides. A low value of Fe_o / Fe_d indicates Fe oxides with a high degree of crystallization or aging (Blume and Schwertmann, 1969; Weisenborn, 2001), while a high value from this ratio indicates Fe is in a more "active" noncrystalline form that is complexed either organically or inorganically (Weisenborn, 2001).

The molar ratio of Fe_p / Al_p is the difference between organically complexed, noncrystalline Fe and Al (Barrett, 1995; Gustafsson et al., 1995). Ratio values less than one signify there is more organically complexed, noncrystalline Al than Fe in that horizon (Weisenborn, 2001), while a ratio of greater than 0.5 could indicate that imogolite is not likely to form due to insufficient Al (Huang, 1991).

The noncrystalline, organically complexed forms of Fe and Al versus the noncrystalline, inorganic complexed forms of Fe and Al in a horizon may be estimated by $(Fe_o - Fe_p) / Fe_p$ and $(Al_o - Al_p) / Al_p$ (Wang et al., 1986; Wang and Kodama, 1986;

Schaetzl, 1992). Higher calculated values signify that inorganic complexes contribute more than organic complexes to the state of Fe and Al in the soil. Conversely, lower calculated values emphasize the role of organic complexes over inorganic complexes.

The relative amount of crystalline "free" oxides compared to noncrystalline "free" oxides may be determined by the difference between the CD value and the AAO value (McKeague et al., 1971; Parfitt and Childs, 1988). When the CD values are larger than the AAO values, crystalline oxides are present (Parfitt and Childs, 1988). Thus, this calculation can, under favorable circumstances, be used to estimate the Fe in goethite, lepidocrocite, and hematite (Parfitt and Childs, 1988; McKeague et al., 1971). The value is negative when the AAO extracts a large amount of "active" noncrystalline oxides and organically bound noncrystalline forms, and which exceeds the CD extracted "free" value. Thus, a low, or negative, value indicates that the "free" oxides are predominantly in noncrystalline form (McKeague et al., 1971).

CHAPTER 5

Study Area

Site Location and Description

The study area for this research was located in the northern Michigan county of Kalkaska (Figure 10). Three of the four sites chosen for this study were within Blue Lake Township; the fourth site was in neighboring Bear Lake Township (Figure 11). All of the sites were located on the sandur east of the Outer Port Huron moraine (Figure 12). Three soil series are present at the four sampling sites; these are the Grayling, Rubicon, and Kalkaska series.

Site Selection Criteria

The four sites used in this research were chosen based on several criteria intended to constrain the soil-forming factors, which are: climate, organics or biota, relief or topography, parent material, and time (Jenny 1941, as cited in Birkeland, 1999). Two of these factors (climate and organics) are active (dynamic, in that they can change with time) in the soil forming process and really cannot be constrained. Even though these factors cannot be fully constrained, their effects were constrained, and between-site variation in these factors was held to a minimum by choosing sites that were in close proximity to one another. The passive factors (relief, parent material, and time) were accounted for by holding them as constant as possible among the sites.

Due to the higher elevations of the moraine, this region is within a major lake effect snowbelt (Schaetzl, 2002). As previously stated, in order to minimize the effects



Figure 10. A map of counties in lower Michigan with Kalkaska County highlighted.

		Site 1		
Clearwater Township	Rapid River Township	Cold Springs Township	Site 2 Blue Lake Township Site 3	
Kalkaska Township	ity of Kalkaska	Excelsior Township	Site 4	
Boardman Township	Orange Township	Oliver Township		
Springfield Township		Garfield Township	1	

Figure 11. A map of Kalkaska County townships with research sites indicated. Sites 1, 2, and 3 are in Blue Lake Township, while Site 4 is in Bear Lake Township.



Figure 12. Map of the morainic system (shown in black) of Michigan with a portion of the Outer Port Huron moraine and the study area for this research in north-central Michigan is indicated in red. (This map is public domain, per a personal communication with Dr. Randy Schaetzl.)

of climate, the distance between sites was kept to a minimum.

The soil-forming factor of vegetation could not be fully constrained. Jack pine (*Pinus banksiana*) was primarily found on the Grayling, red (*P. resinosa*) and white pine (*P. strobus*) were found on the Rubicon, and hardwood, such as sugar maple (*Acer saccharum*) and yellow birch (*Betula allegheniensis*), was found on the Kalkaska sites. The type of vegetation present could be due to the soil's capacity to hold water, which increases with more strongly developed soils (Shetron, 1974; Mokma and Evans, 2000). It could also be due to the history of fire (Schaetzl, 1994, 2002; Barrett, 1997). Vegetation-soil co-occurrences in the region are widespread (Mokma and Vance, 1989). The vegetation patterns are temporal and shift, so it cannot be definitively stated whether vegetation is acting as a dependent or independent variable in soil development in this region (Schaetzl, 2002).

Relief was constrained by choosing sites where the ground slope at the pit was 0-3%. Due to the relief, all the sites are well drained with no water table.

Differences in the parent material were constrained by choosing sites that were all located on the sandur east of the Outer Port Huron moraine (Figure 12). This moraine was formed by the Lake Michigan Lobe, whose ice was mainly from the Superior east area of the Canadian Shield and flowed southwestward across a region north of Lake Huron, then into southern Michigan (Figure 13) (Dworkin et al., 1985). The sediments in this area are almost all glaciofluvial sand or gravel with some glaciolacustrine silt and clay; till is very rare (Blewett et al., 1993). All of the sediments were deposited by glacial meltwater during the retreat of the Port Huron readvance. Some of the sediments may have been reworked by meteoric runoff and post-glacial streams (Schaetzl, 2002).



Figure 13. Map showing the ice movement over the Great Lakes region during the Wisconsin glacial stage. The arrows indicate ice flow and the dashed lines indicate ice lobe boundaries. The Outer Port Huron moraine was deposited by the Lake Michigan Lobe, which flowed southward from the Superior east area of the Canadian Shield (modified from Dworkin et al., 1985).

By choosing sites on the same deposit and in close proximity to one another, age was also constrained. The Outer Port Huron moraine contains some of the youngest Late Wisconsin deposits in southern Michigan (Blewett, 1990). The age of the morainic system was estimated at $12,960 \pm 350$ yr B.P. (Blewett et al., 1993; Schaetzl, 2002).

Based on the above-mentioned criteria, four soils from the Spodosol order were chosen (Figure 11). Site 1 is a soil from the Kalkaska series, which is a strongly developed Spodosol. Sites 2 and 3 are from the Rubicon series, which is less developed than the Kalkaska. Site 2 is a strong Rubicon, while site 3 is a weak Rubicon. Site 4 is from the Grayling series and is the least developed of the soils sampled.

CHAPTER 6

Methods

Sample Preparation

The samples that were used in this research were gathered from four soil pits dug in Kalkaska County (Figures 10 and 11). The pits were dug with a backhoe, and the soils classified based on field observations. Approximately 4kg of soil were taken from each identified pedogenic horizon. The samples were air dried and sieved through an 8mm sieve to remove gravel and larger organics such as twigs and leaves. The samples were then split to obtain 1kg of sample. A soil splitter was used to ensure the sample used in testing was representative of the whole. The grain size distribution was determined for each pedon by Laura Beeman using particle size analysis, following standard laboratory procedures (Soil Survey Division Staff, 1993) (Schaetzl, 2002). The soil pH for each horizon was measured with a model #720A Orion pH meter using a 2:1 slurry of distilled water to soil. The clays were dispersed by soaking and shaking the sample overnight in a solution of sodium hexametaphosphate ([NaPO₃]₆•Na₂CO₃) and distilled water. The sample was then wet sieved through a 53µm sieve. The samples were then placed in a bath of 3% sodium hypochlorite (NaOCl) to remove organic matter, rinsed with distilled water, and dried in an oven at 105°C. The samples were then sieved to obtain the fine sand, or 125µm-250µm, size fraction; this was the size fraction used for this research because the heavy minerals are concentrated in this size fraction (following Locke, 1979; Hall and Horn, 1993).

Hornblende Denticulation Amplitude Determination

The heavy fraction of the fine sand, which includes hornblende, was separated from the cleaned sample by heavy liquid separation. Approximately 42g of each sample were suspended in approximately 50mL of sodium polytungstate $(3Na_2WO_4 \bullet 9WO_3 \bullet H_2O)$, which had been mixed with distilled water (following the manufacturer's instructions) to obtain a specific gravity of 2.95. Hornblende, having a specific gravity of 2.9 – 3.3 (Blackburn and Dennen, 1988), sank to the bottom of the separatory funnel and was easily extracted.

The denticulation amplitude was then determined for 300 hornblende grains from each horizon. This quantity was chosen because of the high confidence limit it provides while allowing a large number of samples to be analyzed in a timely manner (Van der Plas and Tobi, 1965; Pettijohn et al., 1973). The hornblende grains were placed on a glass slide and viewed under a petrographic microscope at 200x. Immersion oil with a refractive index of 1.5 was used to aid in the viewing of the grains at this magnification (hornblende has a refractive index of 1.679 - 1.698 (Klein and Hurlbut, 1999)). To measure the denticulation amplitude, a graded ocular was used in which one scale division equals 4µm.

Hornblende Classification Scheme

Based on amplitude, the grains were assigned a classification that was modeled after the classification scheme of Locke (1979) (Figure 14). Grains that showed no apparent etching were assigned Class 0 (Figure 15). Class 1 indicates etching was present but was less than $4\mu m$ in depth (Figure 16). Class 2 indicates the grains with

etching greater than $4\mu m$ but less than $8\mu m$ (Figure 17). Class 3 had etching greater than $8\mu m$ but less than $12\mu m$, and so on (Figures 18 - 23). For statistical analysis the mean value of the depth of etching in each class was used. Class 0 was assigned a value of 0. Class 1 was assigned a value of $2\mu m$; in class 2 the value was $6\mu m$; and in class 3, $10\mu m$; and so on. These values were then used to calculate a weighted average of denticulation amplitude for each horizon. This was accomplished by multiplying the class value times the number of grains in that class, summing these products, then dividing that sum by the total number of grains counted, which was 300 per horizon.

Unexpected Etching Features

Unexpected etching features were observed while examining grains from the A and E horizons of the Kalkaska, strong Rubicon, and weak Rubicon pedons. On the average, 1 - 3 grains from each of these horizons had dissolution holes through the middle of them (Figure 24). These holes may reflect hornblende dissolution around inclusions, and/or removal of inclusions. Other grains from these same horizons, except for the E horizon of the weak Rubicon pedon, had dissolution features that caused the grains to appear as though they were fracturing (Figure 25). Dissolution at multiple dislocations arrayed in a plane could also produce this corrosion form: side-to-side coalescences of en echelon etch pits is known to form such features (Berner and Schott, 1982; Velbel, 1989). Several grains exhibited both the dissolution hole and fracture feature (Figure 26). A method for measuring these features was not taken into consideration when designing this study simply because of the lack of knowledge at the time with regard to such features. The research was designed for measurements to be



Figure 14. Diagrammatic etching scale showing progress of etching on broken (left) and rounded (right) faces. Depth of etching is shown by indentation in grain margin and is highlighted by shadow (Figure 2 in Locke, 1979).



_____ 20μm

Figure 15. Class 0. Petrographic micrograph of a hornblende grain with no apparent etching. Image captured with a Pixera digital imaging system.



Figure 16. Class 1. Petrographic micrograph of a hornblende grain with etching between $0\mu m - 4\mu m$. Image captured with a Pixera digital imaging system.



Figure 17. Class 2. Petrographic micrograph of a homblende grain with etching between $4\mu m - 8\mu m$. Image captured with a Pixera digital imaging system.



Figure 18. Class 3. Petrographic micrograph of a hornblende grain with etching between $8\mu m - 12\mu m$. Image captured with a Pixera digital imaging system.



Figure 19. Class 4. Petrographic micrograph of a hornblende grain with etching between 12µm – 16µm. Image captured with a Pixera digital imaging system.



Figure 20. Class 5. Petrographic micrograph of a homblende grain with etching between $16\mu m - 20\mu m$. Image captured with a Pixera digital imaging system.



Figure 21. Class 6. Petrographic micrograph of a hornblende grain with etching between $20\mu m - 24\mu m$. Image captured with a Pixera digital imaging system.



Figure 22. Class 7. Petrographic micrograph of a hornblende grain with etching between $24\mu m - 28\mu m$. Image captured with a Pixera digital imaging system.



Figure 23. Class 8. Petrographic micrograph of a hornblende grain with etching between $28\mu m - 32\mu m$. Image captured with a Pixera digital imaging system.



— 20μm

Figure 24. Petrographic micrographs of weathered hornblende grains with holes. Arrows point to holes. Images captured with a Pixera digital imaging system.



— 20µm

Figure 25. Petrographic micrographs of weathered hornblende grains with fractures. Images captured with a Pixera digital imaging system.



Figure 26. Petrographic micrographs of weathered hornblende grains with both holes and fractures. Images captured with a Pixera digital imaging system.

taken of the denticulated edge of the hornblende in order to determine amplitude and subsequent classification. However, when the amplitude of the denticulated edge was measured and the classification was determined, these grains were most likely placed in a class that underestimated the extent of their weathering. These grains were assigned, on the average, to classes 1-3 based on denticulation amplitude of the grain margin; yet, the amount of dissolution that had to occur in order to produce holes and fracture features is greater than the classification 1-3 would indicate. However, the decision was made to classify these grains based on the original research design. Due to the small number of grains encountered with either of these features, it is doubtful that the results are skewed by virtue of using this classification scheme. Perhaps future studies should take these dissolution features into consideration when designing the research in order to utilize or develop a classification scheme that would better accommodate grains with these unusual features.

Quartz/Feldspar Ratio Determination

The degree of mineral weathering was determined by quantifying the quartz/feldspar ratios in each of the horizons. Approximately 25g of the cleaned, fine sand size fraction of the sample was used from each horizon to prepare thin sections. The samples were impregnated with epoxy and allowed to harden to produce a cube that was then sliced, mounted on microscope slides, and ground to a thickness of approximately 30µm. The thin sections were stained with Alizarin red to help distinguish plagioclase feldspar from quartz. However, both plagioclase and K-feldspar were counted as feldspar for the ratio determination. Point counting was performed on these thin sections to obtain

quartz/feldspar ratios. Only quartz and feldspar grains were counted, other minerals and void spaces were disregarded. A total of 300 grains were counted per horizon. Again, the quantity of 300 was chosen for the optimum combination of accuracy and speed (Van der Plas and Tobi, 1965; Pettijohn et al., 1973).

Iron and Aluminum Extractions

The three extracts that were used in this research are: sodium citrate-dithionite (CD), acidified ammonium-oxalate (AAO), and sodium pyrophosphate (PP). Extractions were performed on the illuvial and eluvial horizons only; the C horizons were not analyzed. The methods, which were used to perform these extractions, were from Weisenborn (2001), which were modifications of methods by Ross and Wang (1993) and Loeppert and Inskeep (1996). The modifications were necessary to obtain a sufficient amount of supernatant to yield detectable and measurable amount of Fe and Al when analyzed by atomic absorption spectrophotometer (AAS).

The supernatants were analyzed for extractable Fe and Al on the flame apparatus of the Perkin-Elmer 5100 PC AAS in the Geochemistry Laboratory at Michigan State University. Weisenborn (2001) developed the method for this analysis by modifying the methods from the Soil Survey Laboratory Staff (1996) and Anonymous (1989). The results were reported in percentages of the analyte cation.

Laboratory-Produced Etching Features

Two points around which this research was designed involve chemical analysis of soils to determine Fe and Al accumulation, and measurement of hornblende denticulation

amplitude. It was thought that CD could be employed in both of these analyses. CD could be one of the extractants used to determine Fe and Al accumulation, and it could be used to "clean up" the hornblende grains to prepare them for visual examination (Jackson et al., 1986). Jackson et al. (1986) describe CD as a good method of Fe removal because it is a strong reducing agent, and has a chelating agent to sequester Fe^{2+} and Fe^{3+} ions. The CD system uses sodium citrate as a chelating agent, sodium dithionite (Na₂S₂O₄) as a reducing agent, and sodium bicarbonate (NaHCO₃, pH 7.3) as a buffer.

During the design of this thesis, the question arose as to the degree to which CD, a strong reducing agent, would attack the hornblende, a ferromagnesian mineral. If CD would reduce and remove any crystalline Fe, it could duplicate or enhance the natural etch-features that were going to be measured visually. Using a petrographic microscope, it is possible to discern and measure features that are approximately 1µm in length. Due to this level of detail, and the importance to this study of accurate amplitude measurements, the question of laboratory-produced features on hornblende grains from soils could not be ignored. In order to answer this question fully it was decided that CD, along with the other laboratory pre-treatments, would be tested on hornblende grains to determine whether or not they would produce any artificial alteration features.

Hornblende from the Michigan State University mineralogy teaching collection was used as the control to test the different pre-treatments. The hornblende was first ground with a mortar and pestle then sieved to obtain a fine sand grain size fraction of $125\mu m - 250\mu m$. The sample was then divided into thirds for treatment. The first third of the sample was not treated. The remainder of the sample was exposed to a clay dispersant ((NaPO₃)₆ + Na₂CO₃) in order to follow the standard sample cleaning process

(Soil Survey Division Staff, 1993). The sample was slowly shaken over night in the solution then rinsed with distilled water and dried in an oven at 85°C. The sample was then split in half for the remaining two treatments. One half was treated with sodium hypochlorite (NaOCl) to simulate the removal of organic matter. Bleach, with 6% available NaOCl, was mixed with distilled water to a concentration of 3% available NaOCl. The hornblende grains were placed in the bleach for approximately 8 hours, rinsed with distilled water, and then dried. The final portion of the sample was treated in sodium citrate-dithionite (Na₃C₆H₅O₇ + 10H₂O + Na₂S₂O₄). The hornblende grains were placed in the refrigerator for 6 hours. The grains were then rinsed with distilled water and dried.

A JEOL JSM-6400V scanning electron microscope (SEM) was used to view the hornblende grains to search for alteration features caused by the pre-treatments. The control hornblende grains, which were untreated, showed smooth freshly exposed surfaces and no etching features (Figures 27 and 28). The grains that were treated with sodium hypochlorite also had smooth surfaces (Figures 29 and 30). There were no signs of alteration or weathering features on these grains. The grains that were treated with sodium citrate-dithionite all contained etch pits and laboratory-produced alteration features (Figures 31 and 32), some of them very large (Figure 33). The edges of the grains were not sharp, but showed signs of alteration (Figures 34 and 35). The surfaces on these grains were not smooth, but showed dissolution features (Figures 36 and 37). The hornblende grains treated with CD were the only grains to show any sign of laboratory-produced alteration.


Figure 27. Scanning electron micrograph of an untreated hornblende grain. Image taken at the Center for Advanced Microscopy at Michigan State University by Leslie Mikesell and Ewa Danielewicz.



Figure 28. Scanning electron micrograph of the indicated area on Figure 27 showing smooth surfaces with no etching features.



Figure 29. Scanning electron micrograph of a hornblende grain treated with sodium hypochlorite. Image taken at the Center for Advanced Microscopy at Michigan State University by Leslie Mikseell and Ewa Danielewicz.



Figure 30. Scanning electron micrograph of the indicated area on Figure 29 showing smooth surfaces with no etching features.



Figure 31. Scanning electron micrograph of a hornblende grain treated with sodium citrate-dithionite. Image taken at the Center for Advanced Microscopy at Michigan State University by Leslie Mikesell and Ewa Danielewicz.



Figure 32. Scanning electron micrograph of the indicated 'Area 1' on Figure 31 showing laboratory-produced alteration features.



Figure 33. Scanning electron micrograph of the indicated 'Area 2' on Figure 31 showing large laboratory-produced alteration feature.



Figure 34. Scanning electron micrograph of a hornblende grain treated with sodium citrate-dithionite. Image taken at the Center for Advanced Microscopy at Michigan State University by Leslie Mikseell and Ewa Danielewicz.



Figure 35. Scanning electron micrograph of the indicated area on Figure 34 showing laboratory-produced alteration at the edges.



Figure 36. Scanning electron micrograph of a hornblende grain treated with sodium citrate-dithionite. Image taken at the Center for Advanced Microscopy at Michigan State University by Leslie Mikesell and Ewa Danielewicz.



Figure 37. Scanning electron micrograph of the indicated area on Figure 36 showing laboratory-produced alteration on surfaces.

The laboratory-produced alteration features raised two major concerns about the results of this study. The first concern was whether the laboratory-produced features are discernable at the petrographic microscope scale. This was a problem because the petrographic microscope would be used to classify the hornblende according to a scheme based on the denticulation amplitude. If the laboratory-produced features were mistaken for natural features and then measured as such, the grain would be classified incorrectly.

Due to these laboratory-produced alteration features, I was also concerned was about the validity of the data from the atomic absorption spectrophotometry (AAS). These data could be skewed by mineral dissolution, which would release Fe and Al into the supernatant for measurement. The values obtained would not accurately reflect the "free" Fe and Al but would also measure the Fe and Al from dissolved hornblende.

It was clear from Figures 31 - 37 that hornblende dissolved in the presence of CD and released Fe and Al into solution. It had to be determined how much Fe and Al was released per a given volume of hornblende, and whether or not it was a large enough amount to skew the results from the AAS.

In order to estimate how much Fe and Al was released, a representative hornblende formula was adopted. The hornblende that is found in Michigan soils was glacially transported from a source area in Canada (Dworkin et al., 1985). There are several studies that provide chemical analyses of hornblende from the Grenville Orogen of Ontario, Canada, which is part of the source area for the sediments in this study (Cureton et al., 1997; Cosca et al., 1991). Averaging the values provided, a representative hornblende formula was derived:

 $K_{0.11}Na_{0.42}Ca_{1.83} (Mg_{1.47}Fe^{3+}{}_{0.62}Fe^{2+}{}_{2.06}Ti_{0.07}Mn_{0.02}Al_{0.75})^{vi} (Al_{1.69}Si_{6.31})^{iv}O_{22}F_{0.02}(OH)_{1.98}$

From this average formula, the molecular weight of hornblende was calculated to be 906.28 g/mol. With a specific gravity of 3.1 g/cm^3 (Klein and Hurlbut, 1999), the molar volume of hornblende is 292.35 cm³/mol. Iron in this formula is 149.68 g/mol, or 16.5% of the total weight. It occupies a volume of 48.28 cm³/mol. Aluminum is 65.84 g/mol, or 7.3% of the total weight, and occupies 21.29 cm³/mol.

The volume of hornblende that can be dissolved in the presence of CD, during the time allotted in the methodology, had to be determined. Stereo pairs were made using pictures from the SEM to estimate the depth of the laboratory-produced etch pits (Figures 38 - 41). The stereo pairs were made by taking two Polaroid pictures of the feature of interest. The feature was centered on the screen, and then the first picture was taken. The stub was tilted 3 degrees then re-centered, and another picture was taken. By placing the pictures side-by-side and using stereoscopes, the depth of etch pits was estimated. An average depth for all etch pits viewed was $0.5\mu m - 1\mu m$.

Several assumptions were made before continuing with the calculations. First, it was assumed, for the sake of calculation, that the grains were all spherical. This makes the volume of the grain much easier to calculate. Also, due to the fact that the natural soil grains of this thesis study are from glacial deposits that have been reworked by meltwater, they tend to have a rounded, sub-spherical shape. The second assumption is that the grains are all 200 μ m in diameter. This number was chosen because it is an intermediate value for the fine sand size fraction (125 μ m – 250 μ m) used in the study. The final assumption is that a shell 1 μ m thick was dissolved from each grain. One micrometer is the largest value in the range of 0.5 μ m – 1.0 μ m, which was observed as the average depth for laboratory-produced features. By using 1 μ m, the amount of



Figure 38. Stereo pair 1. Polaroid pictures of scanning electron images were used to estimate the depth of the laboratory-produced etch pits on the homblende grains that were treated with sodium citrate-dithionite. The feature in the left picture is centered and straight; the right picture is tilted 3 degrees. Images were taken at the Center for Advanced Microscopy at Michigan State University by Leslie Mikesell and Ewa Danielewicz.



Figure 39. Stereo pair 2. Polaroid pictures of scanning electron images were used to estimate the depth of the laboratory-produced etch pits on the homblende grains that were treated with sodium citrate-dithionite. The feature in the left picture is centered and straight; the right picture is tilted 3 degrees. Images were taken at the Center for Advanced Microscopy at Michigan State University by Leslie Mikesell and Ewa Danielewicz.



Figure 40. Stereo pair 3. Polaroid pictures of scanning electron micrographs were used to estimate the depth of the laboratory-produced etch pits on the hornblende grains that were treated with sodium citrate-dithionite. The feature in the left picture is centered and straight; the right picture is tilted 3 degrees. Images were taken at the Center for Advanced Microscopy at Michigan State University by Leslie Mikesell and Ewa Danielewicz.



Figure 41. Stereo pair 4. Polaroid pictures of scanning electron micrographs were used to estimate the depth of the laboratory-produced etch pits on the homblende grains that were treated with sodium citrate-ditionite. The feature in the left picture is centered and straight; the right picture is tilted 3 degrees. Images were taken at the Center for Advanced Microscopy at Michigan State University by Leslie Mikesell and Ewa Danielewicz. material added to solution was over-estimated to give an upper limiting value.

In order to estimate the amount of Fe and Al added to solution by the dissolution of hornblende, several calculations were made. The molecular weight and the assumptions stated above were used to calculate the total volume of a 200 μ m diameter sphere of hornblende to be 2.35x10⁻⁶cm³ with a mass of 7.30x10⁻⁶g. When a 1 μ m shell was subtracted to simulate dissolution, the volume of the sphere dropped to 2.32x10⁻⁶cm³ with a new mass of 7.19x10⁻⁶g. The volume loss was 3.6x10⁻⁸cm³ and the mass loss was 1.12x10⁻⁷g. This was a 1.53% loss of both volume and mass.

In order to determine if this volume and weight loss would affect AAS values from the soils, the percentage of hornblende in a soil sample also needed to be determined. This percentage would be the portion of the soil that would dissolve in CD, thus adding Fe and Al to solution. The percent of hornblende in the soil samples collected for this thesis study was determined by performing grain counts (Table 1). Using this percent value, calculations were made to determine the amount of Fe and Al that could be added to solution from hornblende for each horizon. These calculated values were then compared to the actual values of Fe and Al that were obtained by AAS (Table 1). The amount of Fe and Al that could be in solution due to CD dissolution of hornblende was negligible. According to calculations, only 3.6×10^{-8} cm³ or 1.12×10^{-7} g would be lost when a 1µm shell of hornblende dissolved from a 200µm sphere. This would release 1.8×10^{-8} g of Fe and 8.0×10^{-9} g of Al per 7.30×10^{-6} g of hornblende. The amount of Fe and Al that was measured using AAS was significantly higher than the amount of Fe and Al that could be added by the dissolution of hornblende. The AAS measurements were one order of magnitude larger than the calculated values for 13 of the

Table 1. Pedon Data for Laboratory-Produced Alteration Features

Pedon	Soil	Sample	Hornblende	Fe (%) in	Fe (%)	Al (%) in	Al (%)
	horizon	weight	(%) in fine	dry sample	due to CD	dry sample	due to CD
		(g)	grain sample	AA value	dissolution	AA value	dissolution

Kalkaska

Α	1.54	no data	0.067	no data	0.015	no data
E	1.59	2.5	0.052	0.010	0.013	0.004
Bhs	1.52	3.7	0.748	0.014	0.145	0.006
Bs1	1.52	2.2	0.160	0.008	0.183	0.004
Bs2	1.53	1.5	0.054	0.006	0.059	0.003
Bw	1.50	no data	0.045	no data	0.045	no data

Strong Rubicon

Α	1.56	no data	0.085	no data	0.027	no data
Е	1.52	2.2	0.080	0.008	0.017	0.004
Bs1	1.50	6.5	0.696	0.025	0.264	0.011
Bs2	1.53	4.7	0.328	0.018	0.179	0.008

Weak Rubicon

Α	1.60	no data	0.040	no data	0.017	no data
Е	1.50	3.3	0.036	0.012	0.008	0.005
Bs1	1.59	3.3	0.286	0.013	0.176	0.006
Bs2	1.64	4.0	0.049	0.017	0.065	0.007

Grayling

Α	1.58	4.3	0.059	0.017	0.021	0.008
Bs	1.52	5.3	0.108	0.020	0.111	0.009

	Yellow: Fe comparisons
	Blue: Al comparisons
Orange:	value below valid detection limit

comparisons. It was two orders of magnitude larger for 6 of the comparisons. In the remaining 6 comparisons, the AAS measurements were higher than the calculated values, but not significantly higher. Thus, I concluded that the Fe and Al from the sesquioxide coatings on the soil particles were the dominant contributor to the measured values from the AAS.

The original concern that needed to be addressed was whether the laboratoryproduced features are discernable under a petrographic microscope. This concern, in the context of this thesis study, became moot. The grains used for denticulation amplitude measurements were not cleaned of sesquioxide coating prior to examination. That was deemed unnecessary because the coatings were thin enough that they did not affect the measurements taken. However, for future studies, these laboratory-produced features are a source of potential error that should be addressed. It has been reported that CD does not extract Fe and Al from crystalline minerals (Mehra and Jackson, 1960; McKeague et al., 1971; Ross and Wang, 1993). Ross and Wang (1993) stated that this treatment removes the noncrystalline iron oxides, organically bound Fe and Al, as well as the finely divided hematite, goethite, lepidocrocite, and ferrihydrite. Mehra and Jackson (1960) tested CD against three other methods of iron oxide removal to determine its effectiveness. The other three methods were: (1) sodium sulfide-oxalic acid (Na_2S -NH₄Cl-oxalic acid), at a pH of 3.5-10 (Truog et al., 1937), (2) sodium dithionite in acid system (Na₂S₂O₄-H₂O), at a pH of 3.5 (Deb, 1950), and (3) zinc-ammonium oxalate (Znoxalic acid-NH₄ oxalate), at a pH of 3.6 (Haldane, 1956). It was shown that these three methods attack iron-rich silicate minerals. In their conclusion, Mehra and Jackson (1960) said of CD extractant, "Above all, the treatment has almost no destructive effect on iron

silicate clay mineral." My study, however, showed that CD did produce alteration features on hornblende grains that were discernable and measurable under a petrographic microscope. Therefore, it is not recommended to clean hornblende samples with CD when the objective is to measure denticulation amplitude or other etching features.

CHAPTER 7

Results

Soil Classification

The samples from the four sites were analyzed in the laboratory for various physical properties (Table 2) and chemical properties (Table 3). Using these data, the pedons were then classified based on Keys to Soil Taxonomy (Soil Survey Staff, 1998). Site 1, Kalkaska, was classified as a sandy, mixed, frigid Typic Haplorthod (Schaetzl, 2002) (Figures 42 and 43). This site was the most strongly expressed soil studied, and the only pedon with a Bhs horizon. Site 2, strong Rubicon, is a sandy, mixed, frigid Entic Haplorthod (Schaetzl, 2002) (Figures 44 and 45). Site 3, weak Rubicon, is a sandy, mixed, frigid Typic Haplorthod (Schaetzl, 2002) (Figures 46 and 47). Site 4, Grayling, was classified as a sandy, mixed, frigid Entic Haplorthod (Schaetzl, 2002) (Figures 48 and 49). This was the least expressed soil studied, and it lacked an E horizon. Based on the laboratory tests, the Grayling soil classified as a Rubicon. The site, however, was mapped and field classified as a Grayling. So, in order to minimize confusion, I will continue to refer to site 4 as a Grayling soil. There was a trend in soil development that increased from southeast to northwest with the most strongly developed soil, the Kalkaska, being the farthest northwest. That site is in close proximity to Starvation Lake, where local residents report it is not uncommon to have 60+ cm of snow on the ground during winter. The snowpack decreases slightly to the southeast where the lesserdeveloped soils are located (Schaetzl, 2002).

Horizon Depth	Munsell	Grain Size	ТС
(cm)	Color	Cf VCsCs Ms Fs VFsS C	
	(moist)	per cent by weight	

Table 2 . Physical Properties of Pedons.

Kalkask	a	POD Index of	1.5								
Oi	0-3										
Α	3-16	7.5YR 2/0	0.0	0.7	13.0	52.8	18.5	3.3	11.6	0.0	sand
E	16-24	5YR 4/3	0.0	0.5	15.5	54.1	14.8	2.6	12.4	0.0	sand
Bhs	24-31	5YR 2.5/2	0.0	1.7	12.1	50.2	17.1	2.2	13.2	3.5	c.sand
Bs1	31-58	7.5YR 4/6	0.0	0.8	11.0	58.0	21.9	3.4	4.9	0.0	sand
Bs2	58-85	5YR 5/8	4.0	1.9	16.0	62.5	16.2	0.8	2.5	0.0	sand
Bw	85-128	10YR 4/6	4.0	0.8	7.3	59.3	29.3	1.5	1.8	0.0	sand
2E/Bt	128-160+	10YR 4/6(E)	8.0	1.1	14.1	58.7	21.6	2.6	2.0	0.0	sand
		7.5YR 4/4(Bt)									

Strong Rubicon POD Index of 0

Oi	0-5										
Α	5-9	7.5YR 3/2	2.0	1.4	14.3	52.4	19.0	3.2	9.7	0.0	sand
E	9-18	7.5YR 4/2	2.0	1.3	14.5	52.4	18.8	3.3	8.2	1.4	sand
Bs1	18-28	5YR 4/6	6.0	1.8	16.0	50.2	18.0	4.5	8.8	0.7	sand
Bs2	28-48	7.5YR 4/6	6.0	2.3	11.7	51.6	22.2	5.7	6.5	0.0	sand
BC	48-79	10YR 5/6	8.0	2.6	16.5	60.4	17.9	0.7	2.0	0.0	sand
С	79-170	10YR 6/4	8.0	1.4	14.3	59.4	21.1	2.4	1.4	0.0	sand
2C	170+	10YR 6/3	0.0	0.8	10.0	69.5	17.9	1.1	0.7	0.0	sand

Key

- C f Coarse fragments >2mm
- VC s Very coarse sand 1.0mm 2.0mm
- C s Coarse sand 0.5mm 1.0mm
- M s Medium sand 0.25mm 0.5mm
- Fs Fine sand 0.125mm 0.25mm
- VF s Very fine sand 0.053mm 0.125mm
- S Silt 2µm 50µm
- C Clay ${<}2\mu m$
- T C Texture Class
- c. sand coarse sand

Table 2 (continued). Physical Properties of Pedons.

Horizon Depth	Horizon Depth Munsell			Grain Size							
(cm)	C f	VC s C s	M s	F s	VF s S	C					
		per cent by weight									

Weak R	lubicon	POD Index of	2								
Oi	0-4										
Α	4-9	N 2/0	0.0	0.7	19.7	64.2	11.6	0.6	3.3	0.0	sand
E	9-20	7.5YR 4/2	0.0	0.7	17.5	62.0	13.7	1.2	3.7	1.2	sand
Bs1	20-41	5YR 3/4	0.0	1.0	14.0	63.7	15.4	1.2	4.8	0.0	sand
Bs2	41-62	10YR 4/6	0.0	0.2	10.3	71.5	16.1	0.7	0.1	1.0	sand
BC	62-126	10YR 5/4	1.0	0.1	3.0	65.0	30.7	0.8	0.5	0.0	sand
С	126-165+	10YR 6/4	1.0	0.2	2.6	49.5	46.0	1.4	0.0	0.4	sand

Grayli	ng	POD Index of	f 0								
Oi	0-7										
Α	7-11	7.5YR 3/2	0.0	0.4	12.1	63.8	13.9	0.8	9.0	0.0	sand
Bs	11-36	7.5YR 4/6	0.0	0.2	14.7	64.7	15.8	1.0	3.6	0.0	sand
BC	36-62	10YR 5/6	0.0	1.0	15.3	67.0	15.7	0.4	0.7	0.0	sand
С	62-116	10YR 5/4	2.0	0.2	14.7	72.4	11.9	0.4	0.4	0.0	sand
2C	116-140	10YR 5/3	6.0	1.8	16.4	59.0	20.4	1.3	1.1	0.0	sand
3C	140-165+	10YR 5/3	0.0	0.3	11.5	62.8	23.5	1.3	0.6	0.0	sand

Key

C f - Coarse fragments >2mm

VC s - Very coarse sand 1.0mm - 2.0mm

C s - Coarse sand 0.5mm - 1.0mm

M s - Medium sand 0.25mm - 0.5mm

Fs - Fine sand 0.125mm - 0.25mm

VF s - Very fine sand 0.053mm - 0.125mm

S - Silt 2µm - 50µm

C - Clay ${<}2\mu m$

T C - Texture Class

Horizon	Depth	pН	Fe _d	Fe _p	Fe _o	Al _d	Al _p	Al _o
	(cm)		per cent of dry soil					

Kalkaska

Oi	0-3							
Α	3-16	4.7	0.07	0.02	0.01	0.01	0.01	0.01
Е	16-24	4.2	0.05	0.01	0.01	0.01	0.01	0.01
Bhs	24-31	4.0	0.75	0.17	0.18	0.15	0.14	0.14
Bs1	31-58	6.1	0.16	0.07	0.04	0.18	0.20	0.22
Bs2	58-85	6.6	0.05	0.03	0.02	0.06	0.07	0.10
Bw	85-128	6.7	0.05	0.01	0.01	0.04	0.06	0.08
2E/Bt	128-160+	6.9						

Best Expressed Rubicon

Oi	0-5							
Α	5-9	5.4	0.09	0.03	0.02	0.03	0.03	0.03
E	9-18	6.1	0.08	0.02	0.03	0.02	0.03	0.03
Bs1	18-28	5.7	0.70	0.26	0.17	0.26	0.30	0.30
Bs2	28-48	6.4	0.33	0.08	0.08	0.18	0.20	0.28
BC	48-79	7.1						
С	79-170	7.2						
2C	170+	7.6						

Least Expressed Rubicon

Oi	0-4							
Α	4-9	4.0	0.04	0.01	0.01	0.02	0.02	0.02
E	9-20	6.1	0.04	0.01	0.01	0.01	0.01	0.01
Bs1	20-41	6.1	0.29	0.06	0.06	0.18	0.18	0.24
Bs2	41-62	6.9	0.05	0.02	0.01	0.06	0.07	0.13
BC	62-126	7.2						
С	126-165+	7.5						

Grayling

Oi	0-7							
A	7-11	4.4	0.06	0.05	0.02	0.02	0.03	0.03
Bs	11-36	6.1	0.11	0.07	0.03	0.11	0.13	0.17
BC	36-62	6.9						
С	62-116	7.2						
2C	116-140	7.2						
3C	140-165+	7.3						



Figure 42. The Kalkaska pedon is the most strongly expressed Spodosol in the development sequence of this study. Photo taken by Dr. Randy Schaetzl, Professor, Dept. of Geography, Michigan State University.

Site Name: <u>Kalkaska Pit</u>	Map: <u>Starvation Lake Quadrangle</u>
Location: Sand Lake Road	
Slope at pit (%): <u>0</u> Landform type: <u>0</u>	Outwash plain
Parent material: Outwash, coarse at depth	Elevation: <u>394m</u>
Drainage class: Well drained	Erosion: none
Water table (cm): <u>none</u> Evide	ence of bioturbation: <u>none</u>
Vegetation at site: <u>Sugar maple, Red pine</u>	Yellow birch

Horizon	Horizon Depth (cm)	Moist Color (Munsell)	Structure grade	Consistence
Oi	0 - 3			
Α	3 - 16	7.5YR 2/0	weak granular	moist v friable
E	16 – 24	5YR 4/3	weak granular	moist v friable
Bhs	24 – 31	5YR 2.5/2	medium subangular blocky	moist friable
Bs1	31 – 58	7.5YR 4/6	medium subangular blocky	moist friable
Bs2	58 – 85	7.5YR 5/8	weak subangular blocky	moist v friable
Bw	85 – 128	10YR 4/6	weak subangular blocky	moist v friable
2E/Bt	128 – 160+	10YR 5/3 E 7.5YR 4/4 Bt	weak subangular blocky	moist v friable

Figure 43. Selected information from the Soil Profile Description Sheet of the Kalkaska pedon.



Figure 44. The strong Rubicon pedon is the second best expressed Spodosol in the development sequence of this study. Picture taken by Dr. Randy Schaetzl, Professor, Dept. of Geography, Michigan State University.

Site Name: <u>Strong Rubicon Pit</u> Map: <u>Star</u>	vation Lake Quadrangle
Location: <u>N. Blue Lake Road across from Hassley</u>	Road (private)
Slope at pit (%): <u>0</u> Landform type: <u>Outwash</u>	1 Plain
Parent material: Outwash	Elevation: <u>384m</u>
Drainage class: <u>Excessively well drained</u>	Erosion: <u>none</u>
Water table (cm): <u>none</u> Evidence of b	vioturbation: <u>none</u>
Vegetation at site: <u>White pine stumps, reindeer mo</u>	ss, White birch, Pin cherry, Aspen

Horizon	Horizon Depth (cm)	Moist Color (Munsell)	Structure grade	Consistence
Oi	0 - 5			
A	5 – 9	7.5YR 3/2	weak granular	moist v friable
Е	9 – 18	7.5YR 4/2	weak subangular blocky	moist v friable
Bs1	18 – 28	5YR 4/6	weak subangular blocky	moist v friable
Bs2	28 – 48	7.5YR 4/6	weak subangular blocky	moist v friable
BC	48 – 79	10YR 5/6	s grain subangular blocky	moist friable
C	79 – 170	10YR 6/4	s grain subangular blocky	moist v friable
2C	170+	10YR 6/3	s grain subangular blocky	moist v friable

Figure 45. Selected information from the Soil Profile Description Sheet of the strong Rubicon pedon.



Figure 46. The weak Rubicon pedon is the third best expressed Spodosol in the development sequence of this study. Photo taken by Dr. Randy Schaetzl, Professor, Dept. of Geography, Michigan State University.

Site Name: <u>Weak Rubicon Pit</u>	Map: <u>Fredrick Quadrangle</u>
Location: Deward Road on west side	
Slope at pit (%): <u>0</u> Landform type: <u>Te</u>	errace
Parent material: Outwash	Elevation: <u>355m</u>
Drainage class: <u>Excessively well drained</u>	Erosion: <u>none</u>
Water table (cm): <u>none</u> Evidence	ce of bioturbation: <u>none</u>
Vegetation at site: Red pine, Jack pine, Whit	te pine, White spruce, Red maple, Pin cherry

Vegetation at site: <u>Red pine, Jack pine, White pine, White spruce, Red maple, Pin cherry</u> Blueberry, reindeer moss

Horizon	Horizon Depth (cm)	Moist Color (Munsell)	Structure grade	Consistence
Oi	0 - 4			
А	4 – 9	N 2/0	weak granular	moist v friable
E	9 – 20	7.5YR 4/2	weak medium granular	moist v friable
Bs1	20 - 41	5YR 3/4	weak subangular blocky	moist friable
Bs2	41 – 62	10YR 4/6	s grain subangular blocky	moist v friable
BC	62 – 126	10YR 5/4	s grain subangular blocky	moist v friable
C	126 - 165+	10YR 6/4	s grain subangular blocky	moist v friable

Figure 47. Selected information from the Soil Profile Description Sheet of the weak Rubicon pedon.



Figure 48. The Grayling pedon is the least strongly expressed Spodosol in the development sequence of this study. Photo taken by Dr. Randy Schaetzl, Professor, Dept. of Geography, Michigan State University.

Site Name: <u>Grayling Pit</u>	Map: <u>Lake Margrethe Quadrangle</u>
Location: Goose Creek Road across from	Berkley Road
Slope at pit (%): <u>0</u> Landform type:	Terrace in Goose Creek Valley
Parent material: <u>Outwash</u>	Elevation: <u>351m</u>
Drainage class: <u>Excessively well drained</u>	Erosion: <u>none</u>
Water table (cm): <u>none</u> Evid	ence of bioturbation: <u>none</u>
Vegetation at site: Jack pine, blueberry, p	lanted Red pine, reindeer moss

Horizon	Horizon Depth (cm)	Moist Color (Munsell)	Structure grade	Consistence
Oi	0-7			
А	7 – 11	7.5YR 3/2	weak subangular blocky	moist loose
Bs	11 – 36	7.5YR 4/6	weak subangular blocky	moist v friable
BC	36 - 62	10YR 5/6	s grain subangular blocky	moist loose
С	62 – 116	10YR 5/4	s grain subangular blocky	moist loose
2C	116 – 140	10YR 5/3	s grain subangular blocky	moist loose
3C	140 – 156+	10YR 5/3	s grain subangular blocky	moist loose
Deep 3C	280 - 300+	10YR 5/3	s grain subangular blocky	moist loose

Figure 49. Selected information from the Soil Profile Description Sheet of the Grayling pedon.

Hornblende Denticulation Amplitude

Three hundred hornblende grains from each horizon were examined under a petrographic microscope to determine the denticulation amplitude along the margin of the grain perpendicular to the c-axis (Figure 50). A weighted average of denticulation amplitude and the standard deviation were then calculated for each horizon (Table 4, raw data in Appendix A). The weighted average for each horizon was calculated by multiplying the number of grains in each class of that horizon by the mean amplitude measurement for that class, adding these values together, then dividing the sum by 300, which is the number of grains measured in each horizon. These values were used to create a horizon vs. denticulation amplitude plot for each site (Figure 51). All four sites exhibited the same trend within each profile. The denticulation amplitude increased up profile; denticulation amplitudes were minimal in the C horizons, but were larger in the shallower soil horizons. The range of denticulation amplitude, which is the difference between the highest weighted average and the lowest weighted average in each profile. increased as the strength of soil development increased. The Grayling pedon had a range of 0.39µm - 3.24µm or 2.85µm, and the weak Rubicon was 0.57µm - 5.79µm or 5.22µm. The strong Rubicon had a range of 1.15µm - 7.16µm or 6.01µm, while the Kalkaska pedon was 1.31µm-8.21µm or 6.90µm. The average denticulation amplitude measurement for each individual pedon was calculated by averaging the weighted horizon values (Table 4). The average denticulation amplitude for the Grayling was 1.53 μ m, the weak Rubicon was 2.56 μ m, the strong Rubicon was 3.09 μ m, and the Kalkaska was 3.70µm. All four plots exhibit a break in slope directly above the uppermost B horizon. In the Grayling the break was between the A and Bs1 horizons.



— 20µm

Figure 50. Petrographic micrograph of the denticulated margins of a naturally weathered homblende grain. Image captured with a Pixera imaging system.

Horizon Amplitude Deviation Amplitude Amplitude Weighted Highest Lo	owest
Average Measure Measure Average Averag	verage
<u>Kalkaska</u> 3.70 8.21	1.31
A 8.21 4.10 26 2	
E 7.28 4.06 22 2	
Bhs 3.39 2.47 14 2	
Bsl 2.79 1.92 14 2	
Bs2 2.67 1.82 14 2	
Bw 2.20 1.39 10 0	
2E/Bt 1.74 2.00 14 0	
Deep 2C 1.31 1.43 10 0	
Strong Rubicon 3.09 7.16	1.15
A 7.16 4.53 30 2	
E 5.84 4.00 26 2	
Bs1 2.43 1.44 14 2	
Bs2 1.94 0.87 6 0	
BC 1.77 1.15 10 0	
C 1.36 1.20 6 0	
2C 1.15 1.61 10 0	
<u>Weak Rubicon</u> 2.56 5.79 0	0.57
A 5.79 4.17 26 2	
E 4.73 2.99 14 2	
Bs1 2.28 1.26 14 2	
Bs2 2.04 0.63 6 0	
BC 1.65 0.99 6 0	
C 0.89 1.15 6 0	
Deep C 0.57 1.07 6 0	
<u>Grayling</u> 1.53 3.24 (0.39
A 3.24 2.20 14 2	
Bs 2.23 0.97 6 0	
BC 1.75 1.15 6 0	
C 1.42 1.38 10 0	
2C 1.14 1.57 10 0	
3C 0.53 1.12 6 0	
Deep 3C 0.39 0.93 6 0	

Table 4. Denticulation Amplitude Results



Figure 51. Denticulation amplitude vs. horizon plot for each of the pedons in this study. These plots show the change in the mean denticulation amplitude measurement with change in horizon. Error bars represent 1 standard deviation.

In the other three plots the break was below the E and above the uppermost B horizon.

Quartz/Feldspar Ratios

Horizon vs. quartz/feldspar ratio plots were constructed for each site (Table 5 and Figure 52, raw data in Appendix B). The quartz/feldspar values for the deepest horizons for all sites plot at roughly the same point. The two more weakly developed soils, the Grayling and the weak Rubicon, had similar trends, with no systematic vertical change in the quartz/feldspar ratios. This differs from the two more strongly developed soils, the strong Rubicon and the Kalkaska, which plotted similarly to one another exhibiting an irregular but unmistakable increase in the quartz/feldspar ratios up profile.

Extractable Iron and Aluminum

Three extractants were used in this study to determine where Fe and Al were enriched or depleted, and to determine the form of the Fe and Al in each horizon. Fe_d data, which indicate the presence of organically complexed Fe as well as "free" Fe, was at maximum in the horizon immediately below the E horizon in the Kalkaska pedon and both Rubicon pedons (Table 3). The Grayling pedon does not exhibit an E horizon, but the Fe_d is at maximum abundance in the Bs horizon, which is the uppermost B horizon. Al_d data mimic the Fe_d trend in each profile, except in the Kalkaska pedon. Al_d is at maximum abundance in the Bs1 horizon, which is the second B horizon, not the uppermost B horizon.

The PP extractant (Fe_p, Al_p), which extracts Fe and Al from organic complexes, shows a maximum abundance of both Fe and Al in the uppermost B horizon for all pedons (Table 3).

Table 5. Quartz / Feldspar Ratios

Soil &	Quartz / Feldspar
Horizon	Ratios

<u>Kalkaska</u>

Α	15.67
E	16.65
Bhs	8.38
Bs1	11.00
Bs2	5.98
Bw	9.34
2E/Bt	7.33
Deep 2C	6.32

Strong Rubicon

24.00	Α
11.50	Е
16.65	Bsl
10.54	Bs2
16.65	BC
9.71	С
6.14	2C
10.54 16.65 9.71 6.14	Bs2 BC C 2C

Weak Rubicon

Α	5.67
E	7.82
Bs1	6.32
Bs2	4.45
BC	6.69
С	4.56
Deep C	7.11

Grayling

Α	5.25
Bs	6.50
BC	6.14
С	8.38
2C	10.54
3C	8.68
Deep 3C	7.57



Figure 52. Horizon vs. Quartz/Feldspar Ratio. Numbers were used as horizon designations instead of traditional horizon nomenclature because each pedon has various horizon orders. This plot shows the change in the quartz/feldspar ratio with depth.

 Fe_o and Al_o data, which are a measure of the "active" Fe and Al of noncrystalline hydrous oxides, are at maximum in the uppermost B horizon in each pedon, except the Kalkaska pedon where Al_o is at maximum in the Bs1 horizon (Table 3).

Various calculations were made with the extraction data (Table 6). These calculations provide more information as to the nature of the Fe and Al in each horizon (Appendix C). The activity ratio is calculated by AAO / CD (Fe_o / Fe_d) and indicates the amount of crystalline Fe oxides in the soil. A low ratio indicates a large amount of crystalline Fe oxides. The A horizon of the Kalkaska pedon had the lowest ratio, which was calculated to be 0.14. The other ratios were moderately high between 0.20 and 0.40, with the highest ratio being 0.40 from the Bs2 horizon of the Kalkaska pedon.

The calculation that indicates whether the "free" oxides are in a crystalline form or noncrystalline form is CD – AAO (Fe_d – Fe_o and Al_d – Al_o) (Table 6). Low values from this calculation indicate the oxides are primarily in a noncrystalline form. The values for Fe_d – Fe_o are moderately low and range from 0.03 to 0.57. The values for Al_d – Al_o are negative, except for one positive value of 0.01 in the Bhs horizon of the Kalkaska pedon.

The molar ratio of Fe_p / Al_p signifies the difference between Fe and Al in the organically complexed, noncrystalline form (Table 6). Ratio values less than 1.0 signify that there is more organically complexed, noncrystalline Al than Fe in the horizon. The Kalkaska pedon has values greater than 1.0 in the A, E, and Bhs horizons, while the Bs1, Bs2 and Bw horizons have values less than 1.0. The strong Rubicon has a value equal to 1.0 in the A horizon are less than 1.0. However, the weak Rubicon has a value equal to 1.0 in the E horizon, while the A, Bs1, and Bs2
Table 6. Fe and Al Extraction Calculations

Horizon	Fe _o /Fe _d	Fe _d -Fe _o	$Al_d - Al_o$	$\mathrm{Fe}_{\mathrm{p}}/\mathrm{Al}_{\mathrm{p}}$	(Fe _o -Fe _p)/Fe _p	$(Al_o - Al_p)/Al_p$				
	percent of dry soil									

Kalkaska

A	0.14	0.06	0	2.00	-0.50	0
Е	0.20	0.04	0	1.00	0	0
Bhs	0.24	0.57	0.01	1.20	0.06	0
Bs1	0.25	0.12	-0.04	0.35	-0.43	0.10
Bs2	0.40	0.03	-0.04	0.43	-0.33	0.43
Bw	0.20	0.04	-0.04	0.17	0	0.33

Strong Rubicon

Α	0.22	0.07	0	1.00	-0.33	0
E	0.38	0.05	-0.01	0.67	0.50	0
Bs1	0.24	0.53	-0.04	0.86	-0.35	0
Bs2	0.24	0.25	-0.01	0.04	0	0.40

Weak Rubicon

Α	0.25	0.03	0	0.50	0	0
E	0.25	0.03	0	1.00	0	0
Bs1	0.21	0.23	-0.06	0.33	0	0.33
Bs2	0.20	0.04	-0.07	0.29	-0.50	0.86

Grayling

A	0.33	0.06	-0.01	1.67	-0.60	0
Bs	0.27	0.07	-0.06	0.54	-0.57	0.31

horizons are less than 1.0. The Grayling pedon has a value greater than 1.0 in the A horizon and a value less than 1.0 in the Bs horizon.

The calculations of $(Fe_o - Fe_p) / Fe_p$ and $(Al_o - Al_p) / Al_p$ indicate whether the Fe and Al are organically bound or inorganically bound in a noncrystalline form (Table 6). Higher values suggest the inorganically bound complexes contribute more to this measurement, while lower values indicate the organically bound complexes are more dominant. In the Kalkaska pedon, the Fe values are low and range from -0.5 to 0.06. While the Al values in the Kalkaska are zero in the A, E, and Bhs horizons, in the remaining three horizons they range from 0.1 to 0.43. The strong Rubicon has Fe values that are either zero or negative, except in the E horizon where the value is 0.5. The Al values for this pedon are zero in the A, E, and Bs1 horizons, while the Bs2 is 0.4. The weak Rubicon has Fe values of zero, except in the Bs2 horizon where the value is -0.5. The Al values for this horizon are zero except for the Bs1 and Bs2 horizons where the values are 0.33 and 0.86 respectively. The Grayling pedon has Fe values that are negative and Al values that are zero and 0.31.

CHAPTER 8

Discussion

Hornblende Denticulation Amplitude

The weighted average, maximum, and minimum denticulation amplitude of hornblende were determined for each horizon within each pedon (Table 4). Hornblende grains were more weathered, as determined by the denticulation amplitude measurements, at the top of the soil profile than at the bottom of the profile in all four sites. The average was smallest in the deepest C horizon sampled and largest in the A horizon for every pedon. The Grayling C horizon average was 0.39µm compared to its A horizon of 3.24µm. The weak Rubicon averages were 0.57µm in the C horizon and 5.79µm in the A horizon. The strong Rubicon averages were 1.15µm and 6.01µm in C and A horizons respectively, while comparable Kalkaska data were 1.31µm in the C horizon compared to 8.21µm in the A horizon.

Standard deviations were calculated on the weighted averages for each horizon within each pedon (Table 4). The standard deviation, which indicates the spread in the data, was largest in the A horizon and became progressively smaller with depth in the profile for each pedon. This trend is to be expected since the more extensively weathered hornblende is in the upper horizons.

While the hornblende denticulation amplitude showed an obvious trend within each profile, the extent of weathering varied between the profiles. This variability directly corresponded with the strength of soil development. The more strongly developed soils had the more extensively weathered hornblende. This was determined by

comparing the minimum, maximum, and average value of denticulation amplitude for each profile, which was calculated from the weighted averages for each horizon (Table 4). The minimum and maximum values of the pedons followed a progression that increased with increasing strength of soil development. The lowest weighted amplitude average for the Grayling, weak Rubicon, strong Rubicon, and Kalkaska were 0.39µm, 0.57µm, 1.15µm, and 1.31µm respectively. The highest weighted averages were 3.24µm, 5.79µm, 7.16µm, and 8.21µm respectively. The profile average denticulation amplitude also corresponded with strength of soil development (Table 4). The average denticulation amplitude for the Grayling was 1.53µm, the weak Rubicon was 2.56µm, the strong Rubicon was 3.09µm, and the Kalkaska was 3.70µm. The ranges of denticulation amplitude, as well as the average amplitudes, all directly correspond with the strength of soil development.

Horizon vs. Hornblende Denticulation Amplitude

A plot of horizon vs. weighted denticulation amplitude average was constructed for the soil profiles (Fig. 51). All four plots exhibit a break in slope directly above the uppermost B horizon. In the Grayling the break was between the A and Bs1 horizons. In the other three plots, the break was below the E and above the uppermost B horizon. A possible explanation for this break in slope is the presence of two acid systems at work in the soil. Ugolini et al. (1977) suggested that soluble organic acids control the pH and the anionic balance in the upper portion of the soil, whereas the lower portion is dominated by a bicarbonate system. They found mobile fulvic acids were reduced by 60 to 70 percent within the B horizons. The uppermost B horizon delineated the lower boundary

of the biopedological compartment that starts at the top of the canopy. The lower compartment extended downward from the uppermost B horizon, and was in contact with groundwater. The pH increased at the boundary between these two systems, which could account for the varying degree of etching.

In the Grayling soil there was a distinct increase in pH from 4.4 to 6.1 between the A and Bs horizons (Table 3), which was the same point at which the horizon vs. denticulation amplitude plot had a distinct break in slope (Figure 51). The pH increased from 4.0 to 6.1 between the A and E horizons in the weak Rubicon soil (Table 3). However, this was not where the horizon vs. denticulation amplitude plot had a break in slope (Figure 51). The break for this plot was between the E and Bs1 horizons, where the pH held constant at 6.1. The strong Rubicon actually had a decrease in pH from 6.1 to 5.7 (Table 3) between the E and Bs1 horizons (Figure 51) where the plot had a break in slope, and then the pH did increase to 6.4 in the Bs2 horizon. The Kalkaska horizon vs. denticulation amplitude plot exhibited a similar trend to that of the strong Rubicon. In the Kalkaska the pH decreased from 4.2 to 4.0 (Table 3) between the E and Bhs horizons where there was a break in slope (Figure 51). However, the pH did increase to 6.1 in the Bs1 horizon.

There was an increase in pH down profile in all four pedons. Only in the Grayling pedon did the increase in pH correspond with the break in slope of the plot. This pH increase did not, however, directly correspond with the break in slope for the other three pedons; the pH increase occurred one horizon below the break in slope. The data did not show strong, convincing evidence that the boundary between the two

systems of acid was the cause for the break in slope on each of the horizon vs. denticulation amplitude plots, however it may be influential.

Influence of pH on Dissolution Rates

It was observed that the pH in the upper section of the pedon, above the distinct change in pH, was between 4 and 5, while the pH in the lowest sample taken was between 6 and 7.5 (Table 3). The difference in pH between the upper and lower intervals was roughly 2 units in all four sites. The hornblende in the upper profile, with the lower pH, was 6 to 10 times more deeply etched than the hornblende in the lower profile, with the higher pH. All of the grains have been at their present location for the same amount of time, so the hornblende in the upper section etched 6 to 10 times faster than the hornblende in the lower section. These empirical data were compared with experimental data from literature. Sverdrup (1990, as cited in Brantley and Chen, 1995) determined a dissolution rate for hornblende, having the composition of

 $Ca_{1.7}Mg_{3.5}Fe_{1.3}Al_{1.4}Si_{6.9}O_{22}(OH)_2$, at various values of pH. At a pH of 4.4, a dissolution rate of 1.58×10^{-14} moles inosilicate/cm²/sec was measured. At a pH of 6.5, the dissolution rate was 2.00×10^{-15} moles inosilicate/cm²/sec. Given these two rates, dissolution at a pH of 4.4 is 7.9 times faster than dissolution at a pH of 6.5. This value lies within the range observed in the empirical data where dissolution rates were 6 to 10 times faster at a pH of 4 to 5 than at a pH of 6 to 7.5. This consistency supports the idea that the variation in hornblende etching in the upper profile is more strongly influenced by variation in pH than in age.

Factors that Influence pH

It has been concluded by many researchers that pH does influence the dissolution rate of primary minerals (Brantley and Chen, 1995, and all references therein). However, there are many factors that influence the pH of a soil, and thus ultimately influence the dissolution rate of primary minerals.

The range in the dissolution rate of hornblende observed in the empirical data could be explained by natural conditions that vary among the pedons, such as organic matter and the presence of clay. Organic matter influences the soil environment in a number of ways. The accumulation of trace metals in the soils has been attributed to the scavenging of organic humic and fulvic acids based on the observed association between organic-rich soils and high metal values (Hoffman and Fletcher, 1981). It is accepted that organic matter strongly influences the mobility of Fe and Al by complexation and thus providing a means of transport for the Fe and Al ions (e.g., Antweiler and Drever, 1983; Mokma and Evans, 2000; Chadwick and Graham, 2000; Ollier and Pain, 1996; Birkeland, 1999).

Several researchers have studied the effects of organic matter on pH (e.g., Antweiler and Drever, 1983; Mast and Drever, 1986; Birkeland, 1999). Antweiler and Drever (1983) found that the presence of organic matter could lower the pH of the pore water, and thus influence the dissolution rates of minerals. In their study they noted that the pH of percolating water ranged from 4.3 to 6.5. Laboratory experiments were conducted on samples from their study area, in the absence of organic compounds, and yielded a pH range of 7.3 to 9.5. In the laboratory samples the Fe and Al concentrations were below detection limits because Fe and Al are not soluble in that range of pH values.

They also noted that organic matter breaks down to form several different acids that react differently in the soil environment. Acids that were found in their study include: humic/fulvic, oxalate, acetate, and formate acids. Propionate, succinate, and malonate were also tentatively identified. Therefore, they concluded that the breakdown of primary minerals is strongly influenced by the presence of organic matter.

Kalkaska Heavy Mineral Grains and Clay

Clay may also have an influence on the dissolution rate of primary minerals. Not only does clay inhibit the pH from lowering in soils (Bloom, 2000; Churchman, 2000), pedogenic clay may attach to grains, fill pore space, and alter water flow patterns (Chadwick and Graham, 2000; Goldberg et al., 2000; Radcliffe and Rasmussen, 2000).

Understanding that clay may have an influence on the dissolution rate of primary minerals, heavy mineral grains from the Kalkaska A, E, Bhs, and Bs1 horizons were viewed in a scanning electron microscope (SEM) in order to view any clay that might be present. The Kalkaska pedon was chosen because of the very distinct pH change from 4.0 to 6.1 that occurs between the Bhs and Bs1 horizons (Table 3). Roughly 15 grains from each horizon were rinsed to remove dust, and heavy liquid separated to make the selection process easier. In order to observe the clay coatings, or coverings, the clay and sesquioxides were not removed. Energy-dispersive spectroscopy (EDS) was used to identify the weathering product.

The grains above the change in pH were markedly different from the grains below the pH change. These differences included: organic material, weathering product chemistry, and weathering product abundance. In horizon A, with a pH of 4.7, there is

very little weathering product present (Figure 53), however, the weathering product that is present was identified as an aluminosilicate, most likely kaolin $(Al_2Si_2O_5(OH)_4)$ (Figure 54). The determination was based on elements identified by EDS. Organics are also present on these grains as determined by EDS analyses that show a high C peak (Figures 55 and 56). Tube-like features (Figures 57 and 58) were also scanned with EDS (Figure 59) and determined to be organic material due to the high C content. In the E horizon, with a pH of 4.2, there is more clay present than in the A horizon, but less organic matter (Figure 60). The weathering product in this horizon was identified as an aluminosilicate (Figure 61). The grains from Bhs horizon, with a pH of 4.0, have notably more clay than the E horizon, but the grains are not completely coated (Figure 62). This weathering product was also an aluminosilicate (Figure 63). There is also more organic matter in this horizon than in the E horizon (Figure 62). The Bs1 horizon has a pH of 6.1 and is the uppermost horizon below the distinct change in pH. In this horizon, the grains are covered extensively with clay (Figure 64), which was determined to be an aluminosilicate (Figure 65). String-like features were observed in this horizon (Figures 66 and 67), however EDS did not show them to contain carbon (Figure 68). They all had the same EDS signature as the weathering product, which was identified as an aluminosilicate. The identity of these features is unknown.

Several observations were made among the horizons. Tungsten was detected with the aluminosilicate in the Bhs and Bs1 horizons (Figures 63, 65, 68). It most likely sorbed to the clay from the heavy liquid, which was sodium polytungstate, during the laboratory procedure to separate the heavy minerals from the sample. Also, upon examining the EDS data, it was noticed that Al increased in abundance with depth



Figure 53. Scanning electron micrograph of a weathered heavy mineral grain from the A horizon of the Kalkaska pedon with very little weathering product. This product is an aluminosilicate. Image taken at the Center for Advanced Microscopy at Michigan State University by Leslie Mikesell and Ewa Danielewicz.



Figure 54. Energy-dispersive spectrograph of the weathering product indicated the by circle in Figure 53. The high Si content with AI and O led to the determination that it is an aluminosilicate. The Au is the signature of the coating used to prepare the grain.



Figure 55. Scanning electron micrograph of a weathered heavy mineral grain from the A horizon of the Kalkaska pedon with organic material present. Image taken at the Center for Advanced Microscopy at Michigan State University by Leslie Mikesell and Ewa Danielewicz.



Figure 56. Energy-dispersive spectrograph of the organic material indicated by the circle in Figure 55 showing high C content. The Au is the signature of the coating used to prepare the grain.



Figure 57. Scanning electron micrograph of a weathered heavy mineral grain from the A horizon of the Kalkaska pedon with tube-like organic material present. Image taken at the Center for Advanced Microscopy at Michigan State University by Leslie Mikesell and Ewa Danielewicz.



Figure 58. Scanning electron micrograph of tube-like organic material indicated by the circle in Figure 57.



Figure 59. Energy-dispersive spectrograph of tube-like organic material indicated by the circle in Figure 57 showing high C content. The Au is the signature of the coating used to prepare the grain.



Figure 60. Scanning electron micrograph of a weathered heavy mineral grain from the E horizon of the Kalkaska pedon with more weathering product than the A horizon. This product is an aluminosilicate. Image taken at the Center for Advanced Microscopy at Michigan State University by Leslie Mikesell and Ewa Danielewicz.



Figure 61. Energy-dispersive spectrograph of the weathering product indicated the by circle in Figure 60. The high Si content with Al and O led to the determination that it is an aluminosilicate. The Au is the signature of the coating used to prepare the grain.



Figure 62. Scanning electron micrograph of a weathered heavy mineral grain from the Bhs horizon of the Kalkaska pedon with more weathering product and organic material than the E horizon. This weathering product is an aluminosilicate. Image taken at the Center for Advanced Microscopy at Michigan State University by Leslie Mikesell and Ewa Danielewicz.



Figure 63. Energy-dispersive spectrograph of the weathering product indicated the by circle in Figure 62. The high Si content with Al and O led to the determination that it is an aluminosilicate. The Au is the signature of the coating used to prepare the grain.



Figure 64. Scanning electron micrograph of a weathered heavy mineral grain from the Bs1 horizon of the Kalkaska pedon with an extensive coating of weathering product. This product is an aluminosilicate. Image taken at the Center for Advanced Microscopy at Michigan State University by Leslie Mikesell and Ewa Danielewicz.



Figure 65. Energy-dispersive spectrograph of the weathering product indicated by the circle in Figure 64. The high Si content with Al and O led to the determination that it is an aluminosilicate. The Au is the signature of the coating used to prepare the grain.



Figure 66. Scanning electron micrograph of a weathered heavy mineral grain from the Bs1 horizon of the Kalkaska pedon with string-like features that were determined to not be organic due to the EDS having the same signature as the weathering product. Image taken at the Center for Advanced Microscopy at Michigan State University by Leslie Mikesell and Ewa Danielewicz.



Figure 67. Scanning electron micrograph of string-like features indicated by the circle in Figure 66.



Figure 68. Energy-dispersive spectrograph of the string-like features indicated the by circle in Figure 66. The features were determined to not be organic due to the EDS having the same signature as the weathering product. The Au is the signature of the coating used to prepare the grain.

(Figures 54, 61, 63, 65). This is to be expected since Al is more soluble at low pH values, allowing it to move more deeply in the profile (Mokma and Evans, 2000). The mobility of the Al allowed aluminosilicates to form lower in the pedon. A marked increase of pedogenic clay on grains, which was observed between the E and Bhs horizons, could indicate altered water flow paths that would affect the dissolution rate of primary mineral (e.g., Dove, 1995; Nugent et al., 1998). The grain size distribution data support this qualitatively observed increase in clay in the Bhs horizon (Table 2). The Bhs horizon of the Kalkaska pedon is 3.5 percent clay, while the other horizons have 0.0 percent clay. It is at this same point, between the E and Bhs horizons of the Kalkaska pedon, that the break in slope is observed in the horizon vs. denticulation amplitude plot (Fig. 51); meaning the dissolution rate above the Bhs horizon is faster than the rate in the Bhs horizon and below. Determining the exact effect clay has on the dissolution rate of primary minerals is beyond the scope of this study, however, the presence of clay does seem to influence the dissolution rate of primary minerals in soils.

Quartz/Feldspar Ratios as a Weathering Indicator

The quartz/feldspar ratio was chosen to determine relative weathering. For this study, a horizon vs. quartz/feldspar ratio plot was constructed for each of the four pedons (Figure 52). A base, or initial, value was determined by calculating a quartz/feldspar ratio for the deepest sample taken. The deepest horizons for all sites plot at roughly the same point. This indicated that the parent material for the four sites is fairly uniform with respect to the quartz and feldspar content. The divergence in the plots from that point was assumedly due to soil development. The two less developed soils, the Grayling and

the weak Rubicon, plotted similarly, and had near vertical trends; the quartz/feldspar ratios were relatively uniform up-profile. Upper horizons in these two pedons were not depleted in feldspar with respect to quartz, indicating they were not extensively weathered. The two more strongly developed soils, the strong Rubicon and the Kalkaska, also plotted similarly to one another. They both had higher ratios up-profile than the first two plots, and they both had many breaks in slope producing a zigzag pattern. The larger ratio value was caused by a depletion of feldspar with respect to quartz, indicating that these two pedons were more extensively weathered than the Grayling and weak Rubicon.

Grain Size and Quartz/Feldspar Ratios

The multiple breaks in slope, or zigzag pattern, on the horizon vs. quartz/feldspar ratio plot may be due to the grain size used for point counting. Point counts were performed on thin sections that contained only the fine sand size fraction (125µm-250µm) of the soil. During the design of this research, it was decided to use the fine sand size fraction throughout the study because several studies show that heavy minerals, which include hornblende, are concentrated here (e.g., Locke, 1979; Hall and Horn, 1993). Quartz and feldspar are present in this size fraction, however, they are light minerals and their abundance may not be accurately represented in this size fraction alone. The point counting did produce data with an obvious overall trend, but the zigzag pattern may be due to choosing a narrow range and small grain size for point counting. Feldspar grains may break apart along cleavage planes when weathering, producing more and smaller grains than the original. These smaller grains would be concentrated in this size fraction and would not be an accurate depiction of the mineral's abundance in the

whole soil. Quartz, on the other hand, is more persistent than feldspar and may not break up into smaller grains during weathering. This could lead to skewed ratios. The trend of the plot is an accurate depiction for the overall trend of the quartz/feldspar ratios in each pedon. The zigzag pattern, however, may be the result of using only the fine sand size fraction of the soil when point counting.

The A horizon of the Kalkaska pedon does not have the highest quartz/feldspar value, which is different than expected. The zigzag pattern of the slope has the Kalkaska and strong Rubicon plots crisscross each other with the Rubicon having the highest value in the A horizon (Figure 52). In examining the data, it was observed that the strong Rubicon has two anomalies in the physical data (Table 2). The pH values for this pedon are more variable than the pH values of the other three pedons. The Kalkaska, weak Rubicon, and the Grayling pedons all have pH values that exhibit a clear trend; that being a trend of decreasing pH values from the A to the E or an upper B horizon, and then increasing with depth. The pH values for the strong Rubicon do not exhibit a clear trend. This pedon also is different from the other three in its grain size distribution. It is the only pedon to have coarse fragments in the upper horizons. The other pedons have coarse fragments in their lower horizons; however, the strong Rubicon has the highest percent of coarse fragments in those horizons. These two anomalies may indicate the composition of the parent material for the strong Rubicon is slightly different than the parent material of the other three soils. A different composition in the parent material would yield different quartz/feldspar ratios. One observation that makes this explanation questionable is that the deepest samples from all four pedons plot at roughly the same point. However, the anomalous grain size distribution alone could yield these

differences. The strong Rubicon has a higher abundance of the coarse fragments than the other pedons; however, the point counts were performed on the fine sand size fraction of the soil. By using a narrow range of grain sizes, this test could give erroneous data for this pedon. Due to the close proximity of the pedons to one another in the field, and the clear and strong trends in the analytical data for both the hornblende denticulation amplitude and the Fe and Al mobility, it was concluded that the quartz/feldspar ratio trends are due to the difference in grain size and not a difference in composition of the parent material.

Changes in the quartz/feldspar ratios indicate bulk mineralogy change. Rai and Kittrick (1989) suggested soils are short-term entities relative to the time required for the dissolution of minerals to the extent that changes in bulk chemistry could be observed. The age of these pedons, approximately 13,000 yr B.P., may simply be too young for this index to yield conclusive trends and results. It is not known which contributes more to the ambiguity in these results, the age of the soil or the grain size fraction used in point counting.

While these plots do not contradict the order of soil development as assessed in the field, they do not support it either. This mineral weathering indicator simply distinguishes between the two least developed pedons and the two more strongly developed pedons. A clear ordering of the four pedons cannot be demonstrated using quartz/feldspar ratios.

Summary

Hornblende denticulation amplitude measurements and soil development both

indicate the same trend. They suggest the order of soil development among the pedons, in increasing strength, is the Grayling pedon, the weak Rubicon pedon, the strong Rubicon pedon, and the Kalkaska pedon. They both show the same clear, strong trends within each pedon and the same convincing trends among pedons. The quartz/feldspar ratios results did not exhibit strong trends due to ambiguity in the data, which was most likely caused by the young age of the soil or the grain size fraction used for point counting. These ratios did, however, indicate that weatherable silicates were less depleted from the less developed Grayling and weak Rubicon pedons, and more depleted from the more developed strong Rubicon and Kalkaska pedons.

CHAPTER 9

Conclusions

Hornblende Denticulation Amplitude

The hornblende denticulation amplitude measurements were plotted and used to conclude that mineral weathering increased up profile. The plots also showed clear trends that were used to determine a relative weathering order for the pedons in this study.

Comparison of Hornblende Denticulation Amplitude and Soil Development

The hornblende denticulation amplitude measurements and the soil development trends were similar both within and among the four pedons. There was a definite trend of the mineral weathering and soil development being less in the lower profile and progressively increasing in intensity up profile. Also, the mineral weathering trend among the pedons mimicked the order of soil development. From these trends, it can be concluded that, as these soils developed, the minerals weathered, and thus weathering and soil development are related and not independent of one another in these soils.

Comparison of Hornblende Denticulation Amplitude and Quartz/Feldspar Ratios

Quartz/feldspar ratios resulted in trends similar to, but not as strong as, those of the denticulation amplitude measurements. The ratios decreased up profile indicating feldspar was weathering more in the upper profile than in the lower profile. This follows the denticulation amplitude trend, but due to the zigzag nature of the ratio plot, the trend is not strong or clear.

Comparison of Soil Development and Quartz/Feldspar Ratios

Attempting to use quartz/feldspar ratios as indicators of soil development may be inappropriate for soils as young as the pedons in this study, which are approximately 13,000 yr B.P. The ratio of quartz/feldspar relies on the depletion of feldspar as compared to quartz, which is not a rapid process. The plots made in this study showed the two least developed soils to be similar, and the two strongest developed soils to be similar to each other but different than the first two. The results did not provide a convincing relative weathering order for the pedons.

Weathering Versus Soil Development

The terms weathering and soil development have occasionally been used interchangeably. This study shows that mineral weathering and soil development do proceed in tandem on the soils of the study area. However, the terms mineral weathering and soil development reflect two different processes. Bland and Rolls (1998) defined weathering as, "the alteration by chemical, mechanical, and biological processes of rock and minerals, at or near the Earth's surface, in response to environmental conditions." Birkeland (1999) defines soil development as, "a qualitative measure of the amount of pedologic change that has taken place in the parent material." These two processes, although usually occurring simultaneously and/or in parallel in regolith, should be named and referred to correctly. Hornblende as an Age Indicator

Hornblende denticulation amplitude, as an age indicator, may not be appropriate to use on older soils. The hornblende in older soils may have reached a steady state denticulation morphology so there would be no significant difference in the denticulation amplitude (Hall and Michaud, 1988). Steady state conditions in older soils may render this tool useless for determining relative weathering. Denticulation amplitude measurements may be useless as an age indicator also due to steady state. Age determination of a soil, or relative ages of multiple soils, would be impossible by denticulation amplitude alone once steady state has been reached. Without significant differences in amplitudes from one soil to another, an age determination cannot be made.

As previously stated, the quartz/feldspar ratio may be an inappropriate soil development indicator for younger soils because of the time requirements needed for a region to show a depletion in feldspar. However, hornblende denticulation amplitude measurements and quartz/feldspar ratios complement each other. Where the quartz/feldspar ratio is not a good development indicator for younger soils, the denticulation amplitude measurements yield convincing conclusions. The opposite is also true, where the denticulation amplitude measurements may become useless due to steady state in older soils, the quartz/feldspar ratios may exhibit strong trends.

Hornblende etching has been studied by many researchers and has been deemed a suitable tool for relative age determination (Clayton, 1979; Hall and Michaud, 1988; Hall and Heiny, 1983; Hall and Martin, 1986; Locke, 1979, 1986). This study, however, demonstrates that soils formed in deposits of the same age can have significant differences in denticulation amplitudes from one pedon to another. The differences

between the end members, the Grayling and Kalkaska pedons, is great enough that a researcher might conclude they were of different ages if hornblende amplitude was used as a relative age indicator in this setting. Hornblende weathers to produce etch features in a predictable manner that is easily recognizable. However, by using these features alone, it is impossible to distinguish intensity of weathering from duration of weathering. Because of this fact, concluding the etch features are due to duration of weathering is an assumption at best and simply wrong at worst. **APPENDICIES**

APPENDIX A

Denticulation Amplitude Measurements Raw Data Table

Pedon and	Class 0	Class 1	Class 2	Class 3	Class 4	Class 5	Class 6	Class 7	Class 8	Tot	Avg	Std
Horizon	MA 0	MA 2	MA 6	MA 10	MA 14	MA 18	MA 22	MA 26	MA 30			Dev
Kalkaska												
A	0	33	132	88	35	8	3	1	0	300	8.21	4.10
E	0	61	128	76	27	5	3	0	0	300	7.28	4.06
Bhs	0	216	67	14	3	0	0	0	0	300	3.39	2.47
Bs1	0	256	34	9	1	0	0	0	0	300	2.73	1.92
Bs2	0	259	33	7	1	0	0	0	0	300	2.67	1.82
Bw	24	251	23	2	0	0	0	0	0	300	2.20	1.39
2E/Bt	101	177	14	7	1	0	0	0	0	300	1.74	2.00
Deep 2C	129	159	11	1	0	0	0	0	0	300	1.31	1.43
Pedon Avg											3.69	
Strong Rubi	con											
А	0	67	137	61	21	8	4	1	1	300	7.16	4.53
E	0	112	120	44	19	3	1	1	0	300	5.84	4.00
Bs1	0	272	25	2	1	0	0	0	0	300	2.43	1.44
Bs2	25	267	8	0	0	0	0	0	0	300	1.94	0.87
BC	55	236	8	1	0	0	0	0	0	300	1.77	1.15
С	110	183	7	0	0	0	0	0	0	300	1.36	1.20
2C	159	128	10	3	0	0	0	0	0	300	1.15	1.61
Pedon Avg											3.09	
Weak Rubic	on											
А	0	117	117	44	14	4	3	1	0	300	5.79	4.17
E	0	139	124	30	7	0	0	0	0	300	4.73	2.99
Bs1	0	283	14	2	1	0	0	0	0	300	2.28	1.26
Bs2	6	288	6	0	0	0	0	0	0	300	2.04	0.63
BC	62	233	5	0	0	0	0	0	0	300	1.65	0.99
С	175	121	4	0	0	0	0	0	0	300	0.89	1.15
Deep C	223	73	4	0	0	0	0	0	0	300	0.57	1.07
Pedon Avg											2.56	
Grayling		_	_	_		_			_			
А	0	219	70	10	1	0	0	0	0	300	3.24	2.20
Bs	2	280	18	0	0	0	0	0	0	300	2.23	0.97
BC	59	230	11	0	0	0	0	0	0	300	1.75	1.15
С	111	178	10	1	0	0	0	0	0	300	1.42	1.38
2C	163	121	15	1	0	0	0	0	0	300	1.14	1.57
3C	233	61	6	0	0	0	0	0	0	300	0.53	1.12
Deep 3C	248	49	3	0	0	0	0	0	0	300	0.39	0.93
Pedon Avg											1.53	

Key:

MA - Mean amplitude for that class Tot - Total grains measured Avg - Weighted average Std Dev - Standard deviation

APPENDIX B

Quartz and Feldspar Raw Data Table

Soil &	Quartz	Feldspar	Total	Ratios						
Horizon	Counts	Counts	Counts							
Kalkaska										
А	282	18	300	15.67						
E	283	17	300	16.65						
Bhs	268	32	300	8.38						
Bs1	275	25	300	11.00						
Bs2	257	43	300	5.98						
Bw	271	29	300	9.34						
2E/Bt	264	36	300	7.33						
Deep 2C	259	41	300	6.32						
Strong Rubico	n									
A	288	12	300	24.00						
Е	276	24	300	11.50						
Bs1	283	17	300	16.65						
Bs2	274	26	300	10.54						
BC	283	17	300	16.65						
С	272	28	300	9.71						
2C	258	42	300	6.14						
Weak Rubicor	1									
A	255	45	300	5.67						
E	266	34	300	7.82						
Bs1	259	41	300	6.32						
Bs2	245	55	300	4.45						
BC	261	39	300	6.69						
С	246	54	300	4.56						
Deep C	263	37	300	7.11						
Gravling	Gravling									
A	252	48	300	5.25						
Bs	260	40	300	6.50						
BC	258	42	300	6.14						
С	268	32	300	8.38						
2C	274	26	300	10.54						
3C	269	31	300	8.68						
Deep 3C	265	35	300	7.57						

APPENDIX C

Extractable Iron and Aluminum

Podzolization is the process by which Spodosols are developed. During this process, Fe and Al are translocated from the O and A horizons to the B horizons. This process leaves an eluvial zone, or E horizon, which is depleted in Fe and Al, and produces an accumulation of Fe and Al in the B horizons. One measure of strength of soil development is the difference in the amount of Fe and Al in the A and E horizons from that in the B horizons. To determine the amount of Fe and Al that has translocated, Fe and Al were chemically extracted from each of these horizons. In a well developed soil, there should be a trend that exhibits low amounts of Fe and Al in the A and E horizons and a higher amount of Fe and Al in the B horizons, typically with the highest amount in the uppermost B horizon.

Iron and aluminum are found in crystalline, complexes (organic and inorganic), and noncrystalline or amorphous forms in the soil. Three extractions were performed which were designed to test for Fe and Al in these various states. The first extractant was sodium citrate-dithionite (CD), which extracted the "free" Fe and Al. This value represents the total pedogenic crystalline, noncrystalline, and organically bound Fe and Al. The results are denoted as Fe_d and Al_d. The second extractant was acidified ammonium-oxalate (AAO), which is good for indicating the presence of noncrystalline, or amorphous, Fe and Al. The results are denoted as Fe_o and Al_o. The third extractant was sodium pyrophosphate (PP), which is a good indicator for the presence of organically

bound Fe and Al. The results are denoted as Fe_p and Al_p . These values yield a fairly accurate depiction of the movement of Fe and Al within the pedon.

The Fe_d, which indicates the presence of "free" Fe in crystalline, noncrystalline, and organically bound complexes, has its maximum abundance in the horizon immediately below the E horizon in the Kalkaska pedon and both Rubicon pedons (Table 3). This maximum in the uppermost B horizon indicates a translocation of Fe down profile in each pedon. The Grayling pedon does not exhibit an E horizon, but the Fe_d is at maximum abundance in the Bs horizon showing Fe is being eluviated from the A horizon. The Al_d mimics the Fe_d trend in each pedon except in the Kalkaska. The Al_d value is highest in the Bs1 horizon, which is the second B horizon, not the uppermost B horizon. It is common, and almost expected, to have the maximum value for Al occur lower in the pedon than the maximum value for Fe because of the solubility of Al at lower pH values (Mokma and Evans, 2000). These trends show a downward movement of both "free" Fe and Al in all four pedons.

The Fe_o, which indicates the "active" Fe in noncrystalline hydrous oxides, is at maximum abundance in the uppermost B horizon, and has a much lower abundance in the upper horizons of all four pedons (Table 3). The Al_o, which indicates amorphous aluminosilicates, trend is the same as the Al_d trend in that it is highest in the uppermost B horizon in each pedon, except in the Kalkaska pedon where it is highest in the Bs1 horizon. There is a downward movement of "active" Fe and Al in all four pedons.

The Fe_p, which indicates the organically bound, or complexed, Fe, is highest in the uppermost B horizon, and is lower in abundance in the upper horizons (Table 3). The

 Al_p trend is the same as the Al_o and the Al_d . The results from this extractant also suggest a downward movement of Fe and Al.

In examining the data directly, as individual extractions, an accumulation of Fe and Al in the B horizons was observed (Table 3). In all four pedons, the lower values for Fe and Al are in the A and E horizons. The higher values for Fe and Al are in the uppermost B horizon, or in the second B horizon in the case of the Kalkaska pedon, and then the values decrease from that point with depth. Generally, $Fe_d > Fe_p > Fe_o$, which indicates that Fe exists as "free" oxides, either crystalline or noncrystalline, in all four pedons. Also, in all four pedons $Al_o > Al_p > Al_d$ and suggests that Al is primarily "active" noncrystalline.

Various calculations may be made using these values that provide more information about the state of the Fe and Al in the horizon.

The "activity ratio", or Fe_o / Fe_d , for all four pedons yields moderately low values (Table 6). This indicates that Fe is predominantly crystalline in the pedons.

The relative amount of crystalline "free" oxides compared to noncrystalline "free" oxides is calculated by CD – AAO ($Fe_d - Fe_o$ or $Al_d - Al_o$) (Table 6). $Fe_d - Fe_o$ is positive for every horizon in each pedon indicating that crystalline Fe oxide is the primary form of "free" Fe. The $Al_d - Al_o$ value is either zero or negative. One exception to this is the Bhs horizon of the Kalkaska, which is still a low value at 0.01. This indicates that "free" Al is primarily noncrystalline in all four pedons.

The molar value of Fe_p / Al_p signifies whether Fe or Al is more prevalent in the noncrystalline organic complexes (Table 6). Low ratio values indicate more of the complexes are Al than Fe. In the Kalkaska pedon, the A, E, and Bhs horizons have

 Fe_p/Al_p values of one or greater, signifying that Fe complexes are equal to or more prevalent than Al complexes in the upper portion of the pedon; while Fe_p/Al_p in the Bs1, Bs2 and Bw horizons are less than one, indicating that Al complexes are more prevalent in the lower portion of the pedon. This trend could be explained by the solubility and subsequent mobility of Al at these pH values. The A horizon of the strong Rubicon has a Fe_p/Al_p value of one, indicating the number of Fe complexes is roughly equal to Al complexes, while the E, Bs1, and Bs2 horizons have organic complexes mainly of Al. The weak Rubicon has Al complexes more prevalent than Fe complexes in all horizons except the E horizon, where they are roughly equal. The Grayling pedon has mainly Fe complexes in the A horizon and predominantly Al complexes in the Bs horizon. There is an overall trend among the four pedons of higher values in the upper pedon, indicating more Fe complexes than Al complexes, and decreasing values in the lower pedon, indicating Al complexes are more prevalent.

The form of the noncrystalline complexes, whether organic or inorganic, can be estimated by $(Fe_o - Fe_p) / Fe_p$ and $(Al_o - Al_p) / Al_p$ (Table 6). For this calculation, lower values indicate organic complexes are predominant, while higher values indicate inorganic complexes are more prevalent. The values for Fe are zero or negative, suggesting Fe is predominantly organically complexed. This is true for all horizons except in the Kalkaska Bhs horizon where it is 0.06, and in the strong Rubicon where it is 0.50. However, these values are considered low (Wang and Kodama, 1986), indicating Fe is organically complexed in these horizons as well. The values for Al are zero or positive in all horizons. Even with the values being positive, they are still considered low ratio values, indicating Al is also primarily organically complexed. To summarize, the extraction data indicates that Fe and Al in crystalline, noncrystalline, and complexed forms are all moving down the profile. In all four pedons, the Fe is predominantly in "free" crystalline form, meaning it is in Fe oxides. When it is complexed, it is organically complexed. The Al, in all four pedons, is predominantly "active" noncrystalline and organically complexed. Where "free" Al is present, it is also noncrystalline.

It was also observed that the extraction data support the strength of soil development order of the pedons (Table 3 and 5). The Kalkaska pedon exhibits strong, clear trends with maximum values higher than those of any other pedon. This pedon is the only one in which the horizon of maximum Al abundance is below that of maximum Fe abundance, indicating a more strongly developed soil. The strong Rubicon pedon exhibits clear trends, and the maximum values are lower than those of the Kalkaska. The weak Rubicon pedon has trends that are not as clear as the first two pedons, and the maximum values are lower as well. The Grayling pedon does not exhibit an E horizon, indicating it is weakly developed, and so only the A and Bs horizons could be analyzed. These data do, however, show a downward movement of Fe and Al. The extraction data do correlate to the strength of soil development order.

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