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# Parent material and chemical weathering in alpine soils on Mt. Mansfield, Vermont, USA

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#### Abstract

We compared the elemental composition of soil and bedrock samples to determine the extent of chemical weathering and the nature of the soil parent material in alpine soils on Vermont's highest summit. Previously it was unclear whether these soils formed through weathering of bedrock, glacial till, or eolian sediment, or solely through the accumulation of organic matter. In eighteen profiles, no evidence was found to indicate that soils have developed in glacial till, despite evidence that the mountain was completely inundated by the Laurentide Ice Sheet. In contrast, results strongly support the theory that pedogenesis in this environment involves in situ bedrock weathering under a thickening blanket of acidic organic litter. Weathering indices reveal an increase in weathering intensity upwards from the bedrock, and trends of normalized rare earth elements demonstrate a strong similarity between bedrock and soil samples. Leaching has concentrated less mobile elements such as Al, Cr, La, P, Pb, and Ti in soil horizons and removed mobile elements such as Co, Fe, K, Mg, Mn, Si, and Zn. X-ray diffraction reveals that chlorite, which is present in all bedrock samples and some saprolites, has weathered completely from upper soil horizons, and that hydrobiotite, vermiculite, kaolinite, gibbsite, and goethite have formed in the soil. Ratios of immobile elements (Ce, Cr, Nb, Ta, Ti, Y, and Zr) in soil and bedrock samples are, however, notably different. Furthermore, the moderately mobile trace elements Cu, Mo, and Sr are actually more abundant in soil than in bedrock, and soil concentrations of Zr are up to an order-of-magnitude greater than in bedrock samples. Together these data argue for at least a modest eolian influx, which may have arrived during the regression of Lake Vermont during the latest Pleistocene or from an outwash source in the immediate post-glacial period. Similarly, increased Ca and Na concentrations in soil samples may signify modern deposition of dust bearing Ca (from agricultural fields) and Na (from roads). © 2006 Elsevier B.V. All rights reserved.

Keywords: Alpine soils; Pedogenesis; Chemical weathering; Trace elements; Vermont

#### 1. Introduction

Alpine treeline is notably low in the northeastern United States ( $\sim 1200$  m), particularly when compared with mountains at similar latitudes in the western Cordillera ( $\sim 3000$  m). As a result, despite their modest elevation (all < 1920 m) the highest summits in this area support alpine communities featuring a flora common to arctic tundra several hundred kilometers to the north. These environments are remnants of an extensive tundra landscape that dominated the region immediately after deglaciation in the latest Pleistocene. Warming climate during the Pleistocene–Holocene transition

displaced cold-climate communities upward and northward, effectively isolating pockets of tundra atop the highest mountains where climatic and edaphic conditions are too severe for the growth of trees (Zwinger and Willard, 1972; Miller and Spear, 1999).

The aggregate area of alpine tundra in the northeastern U.S. is  $\sim 34 \text{ km}^2$  (Kimball and Weihrauch, 2000). Nearly half of this total is found around Mt. Washington (1917 m asl) in New Hampshire and Mt. Katahdin (1605 m) in northern Maine, with the remainder scattered on lower summits in Maine (Longfellow Mountains), New Hampshire (White Mountains), Vermont (Green Mountains), and northern New York (Adirondack Mountains; Fig. 1A). Yet despite their limited extent these tundra environments have been the focus of considerable study over the past century for several reasons.

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Fig. 1. Location map of the Mt. Mansfield study site. Panel A shows the northeastern U.S. with major alpine areas including Mt. Mansfield (circled MM) and Camels Hump (CH) in Vermont (VT); the Adirondack Mountains (AD) in New York (NY); the White Mountains (WM) in New Hampshire (NH) and Maine (ME); and the Longfellow Mountains (LM) and Mt. Katahdin (MK) in Maine. Panel B presents the topography of Mt. Mansfield (50-m contours) and the major foot trails on the mountain. The arrow points to the study area on the West Chin. The elevation of the summit is 1337 m.

First, their unique botanical assemblages attracted botanists curious about alpine environments and the zonation of plants with altitude (Scudder, 1874; Pease, 1924; Antevs, 1932; Bliss, 1963; Zwinger and Willard, 1972; Ketchledge and Fitzgerald, 1993). Second, conservationists were interested in protecting rare and endemic species such as *Potentilla robbinsiana*, which is found in only two sites in New Hampshire (Cogbill, 1993; Brumback et al., 2004). And third, the surprisingly harsh climatic conditions atop the highest summits provided a relatively accessible location for equipment testing and meteorological monitoring, including ongoing activities at the Mount Washington Weather Observatory (MWO, 2006) and on Whiteface Mountain in New York (ASRC, 2006).

In contrast, it is notable that alpine soils in the northeastern U.S. have been the targets of very little focused study, with

limited work appearing as unpublished graduate theses (e.g. Harries, 1965; Bockheim, 1968; Witty, 1968) and a few papers in the peer-reviewed literature (e.g. Bliss and Woodwell, 1965; Bockheim and Struchtemeyer, 1969; Witty and Arnold, 1970; Ketchledge et al., 1985). Because of this oversight little is known about the properties and genesis of alpine soils in this region. Some of the popular field guides to these environments describe the soils as thin and organic-rich (e.g. Bazilchuk and Strimbeck, 1999), and that cursory statement combined with the exposures visible along hiking trails yields the impression that these soils form solely through the accumulation of organic matter, that bedrock weathering is absent (or of minimal importance) in these environments, and that the chemical and nutrient composition of these soils is unrelated to the mineralogy of the underlying bedrock. Yet recent studies have revealed the importance of chemical weathering in locations with similarly harsh climates (e.g. Caine and Thurman, 1990; Allen et al., 2001; Dixon et al., 2002; Darmody et al., 2005; Dixon and Thorn, 2005), and consideration of the physical setting of alpine soils in the northeastern U.S. suggests four possible pedogenic pathways: (1) soils could be forming solely through the accumulation of organic matter; (2) soils could be forming through chemical weathering of underlying bedrock, (3) soils could be forming in a layer of glacial till overlying the bedrock, and (4) soils could be forming in eolian sediment.

This project evaluates these possibilities, which are not necessarily mutually exclusive, by comparing the chemistry and mineralogy of bedrock and overlying soil horizons in a typical northeastern U.S. alpine zone on Mt. Mansfield in Vermont. The study is one of the first steps in a dedicated program of field and laboratory investigations designed to elucidate the properties of soils in each of the major alpine areas of the region. Work was focused on Mt. Mansfield because alpine soils in Vermont have not been formally investigated, because the mountain supports the largest alpine zone in the Green Mountains, and because the alpine zone there receives tremendous recreational use. Up to 40,000 people visit the summit area annually, arriving via a gondola, a toll road, and numerous hiking trails (Stier and McAdow, 1995). Recreation has had a locally severe impact on the alpine environment as illicit off-trail foot traffic leads to rampant soil erosion and the exposure of extensive areas of bare bedrock (Waterman and Waterman, 1989).

Given the vulnerability of these soils to foot traffic and the attractiveness of alpine zones as destinations, the potential for negative recreation impacts will only continue to increase. And if more areas of alpine tundra are eroded to bare bedrock, then there is great risk that the unique plants of the alpine zone will be extirpated from this region. It is imperative, therefore, to develop management strategies built upon a solid foundation of field-based science to ensure the preservation of these soils. This study aids this effort by identifying the nature of the parent material for these soils and evaluating the role of chemical weathering in their evolution.

## 2. Setting

Mt. Mansfield is the highest summit in Vermont (1337 m). The mean annual temperature (1973 to 1992) at 1190 m on the mountain is 1.4 °C, the mean annual precipitation is  $\sim$  1800 mm, and the mean maximum snowdepth is 215 cm (Wright, 2006). It should be noted, however, that these measurements were taken within the uppermost extent of the subalpine forest, and are not necessarily representative of conditions above treeline (c.f. Bowley, 1978). Treeline occurs at an elevation of approximately 1200 m on the northwestern shoulder of the mountain, where winter winds and frequent icing (Ryerson, 1990) encourage a transition from subalpine forest to *Vaccinium* heath and *Carex* meadow (Bowley, 1978). Individual *Abies balsamea* and *Picea rubens* trees are found at higher elevations, however these form significant clusters in only the most sheltered locations.

Mt. Mansfield, like other summits in the northeastern U.S., was completely overrun by the Laurentide Ice Sheet during the late Pleistocene. Striations, possibly representing two different ice-flow directions (Bowley, 1970), and glacial erratics are present on the summit ridge (Christman, 1959). Cirques eroded by alpine glaciers before arrival of the Laurentide Ice Sheet are found on the eastern and western slopes of the mountain (Davis, 1999). The bedrock is predominantly chlorite-, mica-, and garnet-bearing schist of the Cambrian Underhill Formation (Christman, 1959).

The study site for this project is located south of the main summit of Mt. Mansfield, primarily within the West Chin Protected Area (Fig. 1B). Access to the West Chin area is restricted to authorized researchers in an attempt to reduce impacts to the tundra vegetation. Elevations within the study site average 1310 m, aspects range from 45° to 315°, and slopes range from 0 to 35°.

#### 3. Methods

Because fieldwork for this project was conducted within a protected natural area, considerable effort was made to minimize impacts to the delicate vegetation. Fieldwork was conducted late in the fall, after vegetation was dormant for the winter. Work was also conducted midweek when the number of people on the mountain was at a minimum to reduce the possibility of luring curious hikers off trail. At eighteen locations, randomly selected while pacing a grid designed to determine the variability of soil thickness (Munroe, unpublished data), an  $\sim$ 20-cm diameter pit was excavated to bedrock, and horizons were identified and measured. Bulk samples ( $\sim$ 100 g) were taken from every horizon, and smaller known-volume samples were taken for the determination of bulk density. Samples were also taken of bedrock encountered at the base of each profile. Oa, A, AC, Bw, E, and Cr horizons were identified in profiles that classify as Histosols, Entisols, and Inceptisols (Soil Survey Staff, 2003).

In the laboratory, samples were dried for 2–3 days at 60 °C, then ground with a mortar and pestle, and screened to separate the <2-mm size fraction. Thirty-eight soil and nineteen basal rock samples were submitted to ACME Analytical Laboratories in Vancouver, British Columbia for total elemental analysis by Inductively Coupled Plasma-Emission Spectrometry (ICP-ES) following fluxing with lithium metaborate and nitric acid dissolution.

The average abundances of major and trace elements were compared for soil and rock samples using the non-parametric Mann-Whitney U-test because it is not known whether the population of elemental abundances is normally distributed. Major element abundances results were further investigated through calculation of several weathering ratios taken from the relevant literature (Table 1). For each ratio, oxide weight percents of major elements were first divided by molecular weight to facilitate calculation of molar ratios. Mean values of each index were calculated for Oa/A horizons, Cr horizons, and bedrock; the number of individual examples of other horizons (Bw, AC, E) was insufficient for statistical analysis. Statistical comparison between these means was also accomplished with the Mann-Whitney U-test given the use of ratios and the relatively small number of samples. In all statistical analyses, an  $\alpha$  value of 0.05 was used to determine significance. Finally, ratios of immobile elements in the soil and underlying bedrock were compared to assess the similarity of trace element "fingerprints" in the two materials.

Table 1					
Weathering indices applied to	Alpine	soils	from	Mt.	Mansfield

Formula	Reference		
SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	Ruxton (1968)		
$Al_2O_3/(Al_2O_3 + CaO + Na_2O) \times 100$	Harnois (1988)		
(CaO+MgO+Na <sub>2</sub> O)/TiO <sub>2</sub>	Chittleborough (1991)		
$(SiO_2 + CaO)/(Fe_2O_3 + TiO_2)$	Darmody et al. (2005)		
$(SiO_2+CaO)/(Al_2O_3+Fe_2O_3+TiO_2)$	Darmody et al. (2005)		
SiO <sub>2</sub> /Fe <sub>2</sub> O <sub>3</sub>	Birkeland (1999)		
$SiO_2/(Al_2O_3+Fe_2O_3)$	Birkeland (1999)		
$SiO_2/(Al_2O_3 + Fe_2O_3 + TiO_2)$	Birkeland (1999)		
$(K_2O + Na_2O + CaO + MgO)/Al_2O_3$	Birkeland (1999)		
$(K_2O+Na_2O+CaO+MgO)/(Al_2O_3+Fe_2O_3+TiO_2)$	Birkeland (1999)		
$100 \times (K_2O/0.25 + Na_2O/0.35 + CaO/0.7 + MgO/0.9)$	Parker (1970)		
$100 \times (SiO_2)/(SiO_2 + R_2O_3)$	Reiche (1943)		
	$\begin{tabular}{ c c c c c } \hline Formula \\ \hline SiO_2/Al_2O_3 \\ Al_2O_3/(Al_2O_3+CaO+Na_2O)\times 100 \\ (CaO+MgO+Na_2O)/TiO_2 \\ (SiO_2+CaO)/(Fe_2O_3+TiO_2) \\ (SiO_2+CaO)/(Al_2O_3+Fe_2O_3+TiO_2) \\ SiO_2/Fe_2O_3 \\ SiO_2/(Al_2O_3+Fe_2O_3) \\ SiO_2/(Al_2O_3+Fe_2O_3+TiO_2) \\ (K_2O+Na_2O+CaO+MgO)/Al_2O_3 \\ (K_2O+Na_2O+CaO+MgO)/(Al_2O_3+Fe_2O_3+TiO_2) \\ 100\times (K_2O/0.25+Na_2O/0.35+CaO/0.7+MgO/0.9) \\ 100\times (SiO_2)/(SiO_2+R_2O_3) \\ \hline \end{tabular}$		

able 2	
comparison of mean oxide content of bedrock and soil samples (all horizons)	

					I to Contract	)						
	п	SiO <sub>2</sub> (ppm)	Al <sub>2</sub> O <sub>3</sub> (ppm)	Fe <sub>2</sub> O <sub>3</sub> (ppm)	MgO (ppm)	CaO (ppm)	Na <sub>2</sub> O (ppm)	K <sub>2</sub> O (ppm)	TiO <sub>2</sub> (ppm)	P <sub>2</sub> O <sub>5</sub> (ppm)	MnO (ppm)	Cr <sub>2</sub> O <sub>3</sub> (ppm)
Soil	18	65.6a	20.1b	5.4b	0.7b	0.33b	1.8b	3.5a	1.6b	0.47b	0.12b	0.013b
Rock	35	67.2a	17.8a	7.7a	1.7a	0.22a	1.0a	3.4a	0.8a	0.12a	0.27a	0.010a
Enriched in soil			Х			Х	Х		Х	X		Х
$P(1)^{*}$		0.330	0.034	< 0.001	< 0.001	0.010	< 0.001	0.397	< 0.001	< 0.001	< 0.001	< 0.001
U		339	217	512	578	191	14.5	300.5	1	81	496.5	97.5
Z		-0.44	1.83	-3.69	-4.93	2.32	5.63	0.26	5.89	4.39	-3.4	4.08

\* One-tailed probability from Mann-Whitney U-test.

The mineralogy of rock and soil samples was determined through X-ray diffraction using a Siemens D-500 diffractometer with  $CuK\alpha$  radiation. Whole rock samples were processed with a jaw crusher and a shatter box to create a rock powder. Bulk soil samples were run through a sieve in order to isolate the <2-mm fraction. Quantitative X-ray diffraction (qXRD) analysis was conducted on spray-dried (Hillier, 1999) bulk soil and whole rock samples containing a spike of 10% ZnO as an internal standard (Środoń et al., 2001). Samples were spray dried at 130 °C onto glass slides to ensure random particle orientation. The <2-µm fraction of all bulk soil samples was also isolated through settling after dispersal in deionized water. Samples of the <2-µm fraction were analyzed before and after exposure to ethylene glycol (24 h) to allow identification of expandable minerals. Bulk samples were scanned from  $2^{\circ}$  to  $75^{\circ}$  while the <2- $\mu$ m fraction was scanned from  $2^{\circ}$  to  $40^{\circ}$ . Both types of samples were analyzed at 0.05° steps for 2-s count times.

#### 4. Results

## 4.1. Rock and soil geochemistry

ICP-ES analysis reveals that the bedrock underlying the study area contains an average of 68% SiO<sub>2</sub>, 18% Al<sub>2</sub>O<sub>3</sub>, 8%



Fig. 2. Mean abundance of Rare Earth Elements (REEs) in soil and bedrock samples normalized to a chondrite standard (Nakamura, 1974). Light REEs are enriched by  $\sim 2 \times$  in the soil, while the abundance of other REEs is fairly constant. The overall similarity of the trends supports the theory that the inorganic fraction of the soil is derived from the underlying bedrock.

Fe<sub>2</sub>O<sub>3</sub>, 3.4% K<sub>2</sub>O, 1.7% MgO, and 1.0% Na<sub>2</sub>O. Amounts of CaO, TiO<sub>2</sub>, P<sub>2</sub>O<sub>5</sub>, MnO, and Cr<sub>2</sub>O<sub>3</sub> are all less than 1%. The most abundant trace elements in the bedrock are Ba (mean of 604 ppm), Rb (149 ppm), Zr (141 ppm), V (94 ppm) and Sr (93 ppm). In contrast, the average soil sample contains 66% SiO<sub>2</sub>, 20% Al<sub>2</sub>O<sub>3</sub>, 5% Fe<sub>2</sub>O<sub>3</sub>, 3.5% K<sub>2</sub>O, 1.8% Na<sub>2</sub>O, and 1.6% TiO<sub>2</sub>. Amounts of CaO, MgO, MnO, P<sub>2</sub>O<sub>5</sub>, and Cr<sub>2</sub>O<sub>3</sub> are all less than 1%. Concentrations of Al<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>O, CaO, TiO<sub>2</sub>, P<sub>2</sub>O<sub>5</sub>, and Cr<sub>2</sub>O<sub>3</sub> are, therefore, greater in the soil, while concentrations of other major elements are greater in the bedrock (Table 2). All differences except for SiO<sub>2</sub> and K<sub>2</sub>O are highly significant.

When the concentrations of rare earth elements (REEs) in soil and bedrock samples are normalized to a chondrite standard (Nakamura, 1974) an overall correspondence in the abundance patterns of these elements in the two samples types is obvious (Fig. 2). With the exception of Ce, mean soil values of light REEs are greater by approximately a factor of two. Abundances of the heavier REEs are essentially identical in rock and soil samples.

The most abundant trace elements in the soil are Ba (mean of 630 ppm), Zr (450 ppm), Sr (156 ppm), Rb (143 ppm), and V (118 ppm). Most trace elements are enriched relative to their abundance in the bedrock (Fig. 3). The enrichment is particularly dramatic for Pb ( $7.5 \times$ ), La ( $4.5 \times$ ), and U ( $4.0 \times$ ),



Fig. 3. Ratios of trace elements in soil (n=35) and bedrock (n=18). Ratios >1 indicate enrichment in the soil. Light gray boxes signify elements for which the enrichment is not significant. Enrichment is greatest for Pb, La, and U, while Zn, Ni, and Co have been significantly leached during weathering.



Fig. 4. Ratios of immobile trace elements in soil (n=19) and bedrock (n=36) samples (greater number of samples compared with Fig. 3 reflects inclusion of unpaired samples). Because these elements are all highly immobile under oxidizing and acidic conditions, ratios between the elements should remain constant during weathering, and soils and related bedrock should have similar ratios. However, in all cases, soil and rock samples plot in discrete clusters, suggesting that the soils are receiving trace elements from an extra-local source.

and other trace elements considered immobile under oxidizing and acidic conditions (Kabata-Pendias and Pendias, 1984), such as Bi, Y, Th, and Ta, are also enriched in the soil. In contrast, Co  $(0.1 \times)$ , Ni  $(0.4 \times)$  and Zn  $(0.6 \times)$ , considered to have medium mobility under these conditions, are all diminished relative to the bedrock. Differences between mean concentrations of individual elements in soil and bedrock samples are highly significant except for Au (where a single notably high value elevates the overall soil mean), and Cs, Ba, Rb, Be, and Tl where values are essentially unchanged from bedrock to soil (Fig. 3).

Ratios of immobile elements provide a useful mechanism for identifying multiple parent materials in soil profiles (e.g. Muhs and Benedict, 2006). The concentrations of the most immobile elements should increase during weathering (if surface erosion is negligible), so the relative proportion of immobile elements should be the same in the bedrock and overlying soil horizons if the bedrock is the sole soil parent material. Under the conditions common to the alpine soils in this study, Ce, Cr, Ta, Ti, Y, and Zr should be among the most immobile elements (Kabata-Pendias and Pendias, 1984). Fig. 4 presents the ratios of these different elements in soil (all horizons) and bedrock samples. The range of values for most bedrock samples is greater than for soils, but in general the two sample types plot in non-overlapping distributions with only minimal evidence of mixing.

#### 4.2. Weathering indices

Weathering indices are commonly used in comparing the extent of chemical alteration in different materials (Birkeland, 1999; Darmody et al., 2005). The indices are based on the principle that the ratio between concentrations of mobile (such as SiO<sub>2</sub>, CaO, MgO, and Na<sub>2</sub>O) and immobile elements (Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>) should decrease over time as leaching progresses. Given the formulations of most weathering indices, decreasing values signify greater weathering. The opposite, however, is true for the Chemical Index of Weathering—CIW (Harnois, 1988).

Table 3 presents the mean weathering indices calculated for Oa and A horizons, Cr horizons, and bedrock samples; the number of individual AC, Bw, and E horizons was insufficient to permit statistically robust interpretations. In nine of the twelve indices, weathering intensity increases

Weathering indices cale	culated for alpine	soils from Mt.	Mansfield
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Horizon	n <sup>a</sup>	Si/Al <sup>b</sup>	CIW	WR	WI-1	WI-2	Si/Fe	Si/Ses	Si/R	B/A	B/R	PWI	RPI
Oa/A	19	5.3a	85.8a	2.4a	22.1a	4.3a	38.7a	4.6a	4.3a	0.42a	0.34a	11.5a	80.7a
Cr	6	5.9ab	85.1a	2.6a	25.8a	4.8a	49.5a	5.2a	4.8a	0.45a	0.36a	21.8ab	82.2a
Rock	18	7.2b	89.7b	6.2b	21.2a	5.4a	25.4b	5.6a	5.4a	0.55b	0.41b	23.2b	82.5a

<sup>a</sup> n=number of samples; see Table 1 for definitions of weathering indices.

<sup>b</sup> Different letters designate statistically differentiated clusters ( $\alpha$ =0.05) within a column.

upwards monotonically from the bedrock toward the soil surface. In five of these the difference in mean weathering index of the bedrock and soil was statistically significant. In the remaining indices (CIW, WI-1, and Si/Fe), the bedrock appears more weathered than the Cr horizon, but there is still a trend of increasing weathering (decreasing index in all except CIW) from the Cr to the Oa/A horizon.

#### 4.3. Mineralogy

X-ray diffraction (XRD) patterns are very similar for paired bedrock and soil samples, with the same minerals (mica, quartz, feldspar) dominating each sample type (Fig. 5). The most obvious difference in all samples is the



Fig. 5. X-ray diffraction patterns for a representative soil profile. Panel A displays bulk mineralogy of the Oa and Cr horizons, along with the underlying bedrock (R). Note that chlorite, which is present in the bedrock, is weathering from the soils. Also note the overall similarity of the bulk mineralogy of the soil and bedrock. Panel B shows the <2-µm fraction of the Oa and Cr horizons before (bottom) and after (top) exposure to ethylene glycol for 24 h. None of the peaks exhibit pronounced shifts indicating a lack of well-developed smectite group clays in this particular sample. Kaol is kaolinite, HB is hydrobiotite, Gibb is gibbsite, Qtz is quartz, and Ver is vermiculite. Mica includes biotite and muscovite. ZnO is zinc oxide, added as an internal standard.

presence of chlorite in bedrock and some Cr horizons, but its absence in the overlying soil profile. No exotic mineralogies (i.e. amphiboles, pyroxenes) were encountered in the soil samples. Clay minerals, however, including hydrobiotite, vermiculite, kaolinite and smectite are present in the soil in varying amounts. Gibbsite [Al(OH)<sub>3</sub>] and goethite [FeOOH] are also present in some soil samples.

#### 5. Discussion

### 5.1. Evidence for chemical weathering

Despite the thinness of alpine soils on Mt. Mansfield (generally < 50 cm), and the cold climate under which they form, the geochemistry of soil and bedrock samples provides abundant evidence for chemical weathering. Comparison of the major element chemistry of soil and bedrock samples indicates that mobile elements (Fe, Mg, and Mn) are being leached from the soil while immobile elements (Al, Ti, P, and Cr) are being concentrated. Similar trends are seen in the enrichment of immobile trace elements and the significant leaching of Co, Ni, and Zn. Trends in REE abundance also co-vary for soil and bedrock samples with a predictable enrichment of light REEs in the soil. All of the calculated weathering indices indicate that surface soil horizons are more weathered than Cr horizons, and most indices reveal that surface and subsurface soil horizons are more weathered than the underlying bedrock. Together these results demonstrate that chemical weathering is occurring at the highest elevations on Mt. Mansfield.

The mineralogy results provide additional evidence of chemical weathering in this environment. Chlorite, which is present in all of the bedrock samples, is absent from all of the soil samples above Cr horizons, indicating that it has been completely eliminated by chemical weathering. Secondary clay minerals, including hydrobiotite, vermiculite, and kaolinite have formed in the soil, along with aluminum and iron hydroxides (gibbsite and goethite), and are likely derived from weathering of chlorite and biotite. The presence of gibbsite is notable as evidence for pronounced chemical weathering (April and Newton, 1983). Mineralogical data are consistent with a local bedrock origin of these soils. The presence of chlorite in trace amounts in saprolite (Cr) is consistent with transition from chlorite-rich bedrock to soil that contains no chlorite. Furthermore, similar concentrations of the more stable minerals quartz and plagioclase in rock and soil also strongly suggest that soil is derived from the chemical weathering of underlying bedrock.

The results of this study provide support from a lowerlatitude alpine environment for the conclusions reached by a comprehensive investigation of pedogenesis in the Kärkevagge region of northern Sweden (Darmody et al., 2000; Allen et al., 2001; Dixon et al., 2002; Darmody et al., 2005). Dixon et al. (2004) and Dixon and Thorn (2005) note that chemical weathering is commonly considered subordinate to physical weathering in arctic and alpine environments, despite compelling evidence to the contrary (e.g. Rapp, 1960; Caine and Thurman, 1990; Hall et al., 2002). Yet in Kärkevagge, considerable evidence has been uncovered to support the conclusion that chemical weathering actually plays an important, if not dominant, role in some cold climate weathering regimes. The situation on Mt. Mansfield appears similar, and future work will attempt to expand the strategy employed here to other areas in the northeastern U.S. where alpine soils are found over different bedrock lithologies.

### 5.2. Identity of parent material

The overall geochemistry and mineralogy results allow evaluation of the four possible parent materials for alpine soils on Mt. Mansfield. No erratic clasts were encountered in any of the excavated profiles to indicate that the soils have developed in a layer of glacial till. This result suggests that whatever glacial sediment was originally deposited at the highest elevations was washed away before the landscape became sufficiently stable for pedogenesis. Alternatively, glacial till may never have been deposited at the highest elevations. Theoretical considerations suggest that the amount of supraglacial debris carried by a glacier decreases with increasing landscape denudation (Boulton, 1970), and for Mt. Mansfield to be overrun by ice, the degree of topographic inundation along an up-ice flowline would be 100%. Furthermore, basal ice overrunning the mountain must have first climbed an adverse slope where pressure melting should have led to a dominance of deposition (through basal melting) over entrainment (through regelation) (Paterson, 1994). Basal debris entrainment may, therefore, have been negligible on the immediate up-ice side of Mt. Mansfield, and while the presence of striations and scattered erratic boulders on the summit ridge indicate that the basal ice contained at least some debris, the overall debris content of ice passing over the summit may have been minimal.

In contrast, there is abundant evidence to support the theory that the soils are forming through *in situ* weathering of local bedrock. This is the most parsimonious interpretation of the nearly identical bulk mineralogies of soil and bedrock samples and the parallel REE abundances. The weathering indices indicate that the soil is more weathered than the bedrock, and in almost all indices the intensity of weathering increases towards the surface. Thus it seems likely that the chemical and mineralogical properties of the soil are strongly controlled by the underlying bedrock. A corollary to this argument is that the soils are more than simple mats of decomposing organic matter draped over the bedrock. Instead they appear to derive much of their inorganic components through chemical weathering of minerals in the underlying schist.

Scrutiny of the trace elements results, however, suggests that at least some of the inorganic component of the soil is derived from an extra-local source. For instance, Cu, Mo, and Sr are considered to have medium mobility in oxidizing and acidic environments (Kabata-Pendias and Pendias, 1984), yet all three are enriched in the soil by at least  $1.7 \times$ . Ca and Na are also mobile under these conditions and yet are significantly enriched in the soil (Table 2). Furthermore, Zr is highly immobile under these conditions, but its enrichment in the soil (mean of  $3.2 \times$ , max. of  $10 \times$ ) is so great that it is difficult to explain by weathering-related concentration alone. Finally, the ratio plots (Fig. 4) reveal that the soil and bedrock samples have distinct fingerprints with respect to the most immobile trace elements. Together these results suggest that at least some of the inorganic fraction of the alpine soils on Mt. Mansfield is derived from eolian sediment. Future work will attempt to determine the particle size fraction carrying the exotic trace element signature, which should help test the theory that the exotic trace elements are coming from loess (e.g. Muhs and Benedict, 2006).

Eolian sediment has been shown to play an important role in alpine pedogenesis in the western U.S. (e.g. Liator, 1987; Dahms, 1993; Dahms and Rawlins, 1996; Bockheim et al., 2000; Birkeland et al., 2003; Muhs and Benedict, 2006) where semi-arid lowlands underlain by fine-grained sedimentary rock and late Cenozoic sediment are common in close proximity to upland ranges. In contrast, evidence for eolian sedimentation in alpine zones of the northeastern U.S. is surprising given the humid climate and vegetated state of modern landscape. Dust bearing Ca is produced during spring tilling of agricultural soils in the Champlain Valley upwind of Mt. Mansfield, and Na-bearing salts are applied to many roads in this area during the winter. Thus at least some of the eolian influx may be contemporary. However, given the magnitude of the trace element enrichment and the departure from the trace element fingerprint of the underlying bedrock it seems likely that the majority of the eolian influx occurred as a discrete pulse during a period in which regional conditions were more suitable to dust entrainment, transport, and deposition.

Consideration of the post-glacial history of the northeastern U.S. reveals two possible periods in which these conditions would have prevailed. The first occurred in the late Pleistocene as the margin of the Laurentide Ice Sheet retreated northward. Much has been written about the style of deglaciation in the high-relief landscape of northern New England (see review in Thompson, 1999; Thompson et al., 1999), but there is general consensus that the higher elevations emerged first as nunataks, followed by progressively lower elevations until only residual, locally stagnant, ice was left on valley floors (Goldthwait and Mickelson, 1982). During this period of paraglacial landscape adjustment (Ryder, 1971; Church and Ryder, 1972), there would have been great potential for dust entrainment from outwash surfaces and kame deposits associated with decaying ice masses. The highest elevations, which had been ice-free the longest, may have presented relatively stable locations for dust accumulation in this landscape, especially if colonial plants and lichens were already building nascent soils.

A second pulse of eolian activity may have accompanied the regression of Lake Vermont from the Champlain Valley west of Mt. Mansfield in the latest Pleistocene. This large proglacial lake formed as the retreating ice sheet blocked northward drainage into the St. Lawrence River (see review in Rayburn et al., 2005). When the obstructing ice was removed, the impounded waters were released, exposing an extensive area of former lake bottom covered in fine-grained sediment with an exotic northern provenance.

#### 6. Conclusion

The results of this study indicate that the formation of alpine soils on Mt. Mansfield, VT, involves more than the simple accumulation of non-mineral organic material. Instead, chemical weathering of local bedrock and at least a minor input of eolian sediment appear integral to pedogenesis in this environment. The evidence in support of this interpretation can be summarized as follows:

- Concentrations of immobile major and minor elements are increased in soil compared with the underlying bedrock, while concentrations of mobile elements are reduced. Both trends indicate the operation of leaching, likely enhanced by the considerable annual precipitation (~1800 mm) in this environment.
- Weathering indices based on ratios of mobile to immobile major elements reveal that soil horizons are generally more weathered than underlying bedrock, and that near-surface soil horizons are more weathered than subsurface horizons.
- Trends of normalized rare earth elements (REEs) in soil closely parallel those in the underlying bedrock, with predictable enrichment of light REEs.
- X-ray diffraction indicates that bulk mineralogy of bedrock and soil samples is quite similar and that the major differences can be explained by chemical weathering. Chlorite is present in all rock samples and some saprolites (Cr horizons), but is universally absent from the upper soil samples. In contrast, mixed-layer clays (i.e. hydrobiotite), vermiculite, kaolinite, gibbsite, and goethite have all formed in soil samples.
- No exotic mineralogies or erratics were found to suggest that soils have formed in glacial till.
- Ratios of immobile trace elements in bedrock samples are distinct from those calculated for soils, indicating that at least part of the inorganic component of the soil was not derived from the underlying bedrock. This discrepancy suggests that the soil profiles have been enriched in some trace elements through dust deposition. Additional support for this interpretation comes from the great enrichment in Zr values in the soils (up to 10× over the bedrock) and the concentration of elements (Ca, Cu, M, Na, Sr) considered at least moderately mobile under oxidizing and acidic conditions.

Enrichment of Ca and Na in alpine soils on Mt. Mansfield may reflect contemporary deposition of dust derived from

agricultural fields and roads immediately upwind. However, given the humid climate and vegetated landscape of the northeastern U.S., the majority of the eolian sediment may have accumulated during deglaciation when unvegetated outwash and kame deposits were widespread in the surrounding lowlands, or during the regression of proglacial Lake Vermont during the latest Pleistocene. If this interpretation is correct, then the presence of pre-Holocene dust in alpine soils on Mt. Mansfield indicates that at no time during the post-glacial period was the summit of the mountain stripped to bare bedrock, a situation that may be responsible for the continued existence of arctic-alpine flora on the summit. This revelation highlights the fundamental importance of soils as a foundation for the unique arcticalpine refugia of this region's highest summits, and lends support to efforts designed to manage recreational impacts in these fragile environments.

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