

Substrate Geochemistry and Soil Development in Boreal Forest and Tundra Ecosystems in the Yukon–Tanana Upland and Seward Peninsula, Alaska



Scientific Investigations Report 2008–5010

Cover. View of the middle reaches of the Tibbs Creek drainage in the Big Delta B-1 quadrangle, looking west-northwest. Soils in this area of the Yukon-Tanana Upland are mainly Inceptisols that lack permafrost, contain Quaternary loess, and are derived from the weathering of Paleozoic metamorphic and Early Cretaceous granitic rocks. (Photograph by L.P. Gough, U.S. Geological Survey)

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Conversion Factors and Abbreviations

Multiply	By	To obtain
Length		
centimeter (cm)	0.3937	inch (in.)
millimeter (mm)	0.03937	inch (in.)
meter (m)	3.281	foot (ft)
kilometer (km)	0.6214	mile (mi)
Mass		
gram (g)	0.03527	ounce, avoirdupois (oz)
kilogram (kg)	2.205	pound avoirdupois (lb)

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:

$$^{\circ}\text{F}=(1.8\times^{\circ}\text{C})+32$$

Abbreviations used in this report

Ka - thousand years before present

M - molar

Ma - million years before present

mL - milliliter

µm - micrometer

n - number of samples

N - normal

NIST - National Institute of Standards and Technology

R² - square of the correlation coefficient

USGS - U.S. Geological Survey

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Abstract

We report on soil development as a function of bedrock type and the presence of loess in two high latitude ecosystems (boreal forest and tundra) and from two regions in Alaska—the Yukon-Tanana Upland (YTU, east-central Alaska) and the Seward Peninsula (SP, far-west coastal Alaska). This approach to the study of “cold soils” is fundamental to the quantification of regional geochemical landscape patterns. Of the five state factors in this study, bedrock and biota (ecosystem; vegetation zone) vary whereas climate (within each area) and topography are controlled. The influence of time is assumed to be controlled, as these soils are thousands of years old (late Quaternary to Holocene).

The primary minerals in soils from YTU, developed over loess and crystalline bedrock (metamorphic and intrusive), are quartz, plagioclase, and 2:1 clays; whereas in the SP, where loess and metasedimentary bedrock (schist and quartzite) predominate, they are quartz and muscovite. The A horizon of both regions is rich in peat. Examination of the ratio of mobile (K_2O , CaO , and Fe_2O_3) to immobile (TiO_2) major oxides, within each region, shows that very little difference exists in the chemical weathering of soils developed between the two ecosystems examined. Differences were observed between tundra soils developed in the two regions. These differences are most probably due to the dissimilarity in the geochemical importance of both loess and bedrock.

A minimal loss of cadmium with soil depth is seen for soils developed over YTU crystalline bedrock in the boreal forest environments. This trend is related to the mobility of cadmium in these soils as well as to its biogenic cycling. Major differences were observed in the proportion of cadmium and zinc among the A, B, and C horizon material sequestered in various soil fractions as measured by sequential soil extractions. These trends followed such variables as the decrease with depth in organic matter, the change in clay minerals, and

the change in the proportion of oxides/hydroxides. An analysis of the bulk soil mineralogy and the relation between CaO and MgO and Al_2O_3 and Fe_2O_3 indicates that the silty textured soils of the YTU are predominantly eolian (that is, of late Tertiary or Quaternary age) but not broad-regional in origin. Their composition instead is probably the result of locally derived dusts as well as input from long-term, in-place bedrock weathering.

Objective

The objective of the study was to test two alternative hypotheses about high latitude soil weathering: (1) Soils developed from combined loess and uniform bedrock units have different geochemical signatures, depending on the ecosystem where they are formed, versus (2) soils developed where weathering rates are too slow, ecosystem processes are too indistinguishable, or the presence of loess material confounds meaningful differences in the soil geochemical signatures of ecosystems (or vegetation zones). The ecosystems investigated were the boreal forest and tundra (which included Arctic, open alpine, and shrub-tundra).

The following processes and (or) physical characteristics could influence geochemical signatures: (1) bedrock type, (2) age of soil, (3) physical, chemical, and biological weathering rates versus loess deposition rates (Muhs and others, 2004), (4) vegetative cover and organic acid illuviation, (5) aspect and altitude, and (6) depth to permafrost (and drainage efficiency). Through site selection within each region we controlled as many of these variables as possible while varying the bedrock and biota (ecosystem). We realize, however, that some local climatic differences were evident owing to the presence or absence of permafrost and to dissimilarities observed in the depth, thickness, and characteristic of the weathering profiles.

Introduction

Landscape Setting

Several processes affect the development of high latitude (cold) soils and their resultant regional landscape geochemical patterns. We focused on the development of soils over crystalline (metamorphic and intrusive) and metasedimentary (schist and quartzite) bedrock. If ecosystem differences result in soil development differences, then, over time, system perturbations (climate change) could alter regional geochemical landscape patterns. The study areas were the Yukon-Tanana Upland (YTU) located in the Big Delta B-1 and B-2 quadrangles about 200 kilometers (km) east-southeast of Fairbanks and the Seward Peninsula (SP), located in the Nome and Solomon quadrangles in far western Alaska.

The YTU study area (fig. 1) is characterized by rounded, low mountains with scattered sparsely vegetated to barren high peaks. Nowacki and others (2002) classify the area as the Intermontane Boreal Ecoregion. The boreal forest vegetation is composed of closed spruce-hardwood forest containing white and black spruce, paper birch, aspen, and balsam poplar. The tree line is at about 900 meters (m), and above it the alpine tundra zone is composed of low shrubs (willow, birch, blueberry, crowberry) and a ground cover of grasses, forbs, mosses, and lichens. Lightning-caused wildfires are common, and most of our study sites, especially those in forested areas, showed evidence of past fire disturbance. The climate of the area is typical of continental interior Alaska, which is characterized by warm, dry summers, very cold, dry winters, daylight hours that vary from about 4.5 hours in December to 19.5 hours in June, and broad fluctuations in ambient temperature (Van Cleve and Yarie, 1986).

The SP landscape is treeless and rolling with vegetated arctic tundra dominated by shrubs (willow, blueberry, crowberry), herbs, grasses, forbs, lichens, and mosses. The region sampled is characterized by a much lower elevation than YTU (maximum of about 400 m) and possesses short cool, wet summers and cold, dry winters. Soils of this region are less influenced by loess than in the YTU (Muhs and others, 2003a). Nowacki and others (2002) classify this area as the Bering Tundra Ecoregion. The latitude (64° N.) is the same for both SP and YTU (fig. 1).

Soils

The factors that control soil formation (climate, biota, parent material, topography, and time) (Jenny, 1980) are the same factors that have been used by Van Cleve and others (1991) to model the structure and function of the boreal forest biome in Alaska. Except for permafrost areas (Ferrians, 1965),

these soils are ice free for only a few months during the summer, and uppermost horizon temperatures seldom exceed 5° to 10° C. Both chemically and biologically mediated weathering are slow (Campbell and Claridge, 1992). Boreal forest and tundra vegetation produce organic acids, through organic matter decomposition, that accelerate certain soil formation processes (for example, the release of metal cations from silicate minerals and their co-precipitation with Al, Fe, and Mn oxides and hydroxides). An even colder environment, with slower soil microbial activity and less vegetative cover, occurs at higher elevations and latitudes. In these environments the soils usually have fewer organic acids and consequently have even slower soil formation processes. The principal proton donor in these systems is carbonic acid, the product of root respiration (Campbell and Claridge, 1992), which becomes even more soluble in water as temperatures decrease.

The study area soils are late Quaternary to Holocene in age (Muhs and others, 2003b) and developed from both loess and a wide variety of predominantly crystalline and metasedimentary bedrock types (see Geology section below). Soils collected were either Inceptisols (mainly Cryepts or Gelepts) (fig. 2) or Gelisols (mainly Orthels). Spodosols were observed but not collected. These latter soils have abundant organic carbon within the spodic horizon and were usually found only in well-drained areas in white spruce forests. Greater than 30 percent of our sites were near saturation at the time of collection, and permafrost, when present, was commonly observed from 15 to 50 centimeters (cm) below the surface. Our soils can be described broadly as those with and those without permafrost or evidence of permafrost. Those with permafrost were most commonly in areas of tundra overlain with a thick O horizon. The O horizon was composed of cryptogams and abundant plant debris that became more sapric with depth and overlaid the silty loam to fine sandy loam mineralized A1 soil horizon. The A horizon was usually <10 cm in thickness and dark brown in color (indicative of abundant organic matter), with numerous roots, and a few possessed an eluviation (E) horizon (fig. 2). The typical B horizon was usually about as thick as the A horizon, lighter and more reddish in color, and contained moderate root volume. Yellowish C-horizon soils commonly extended below 20 to 40 cm in depth and consisted of silt and fine-to-coarse sand with small blocks of angular bedrock and few roots.

Although boreal and tundra areas differ greatly in the degree of cryoturbation, snow accumulation depths, and vegetative composition, we attempted to maintain consistency within the two major areas sampled (YTU and SP). This consistency resulted in fairly uniform soil horizontal characteristics. What did vary among the sites, however, was the abundance of loess, the presence and amount of bedrock inclusions, and the ranges in soil moisture.

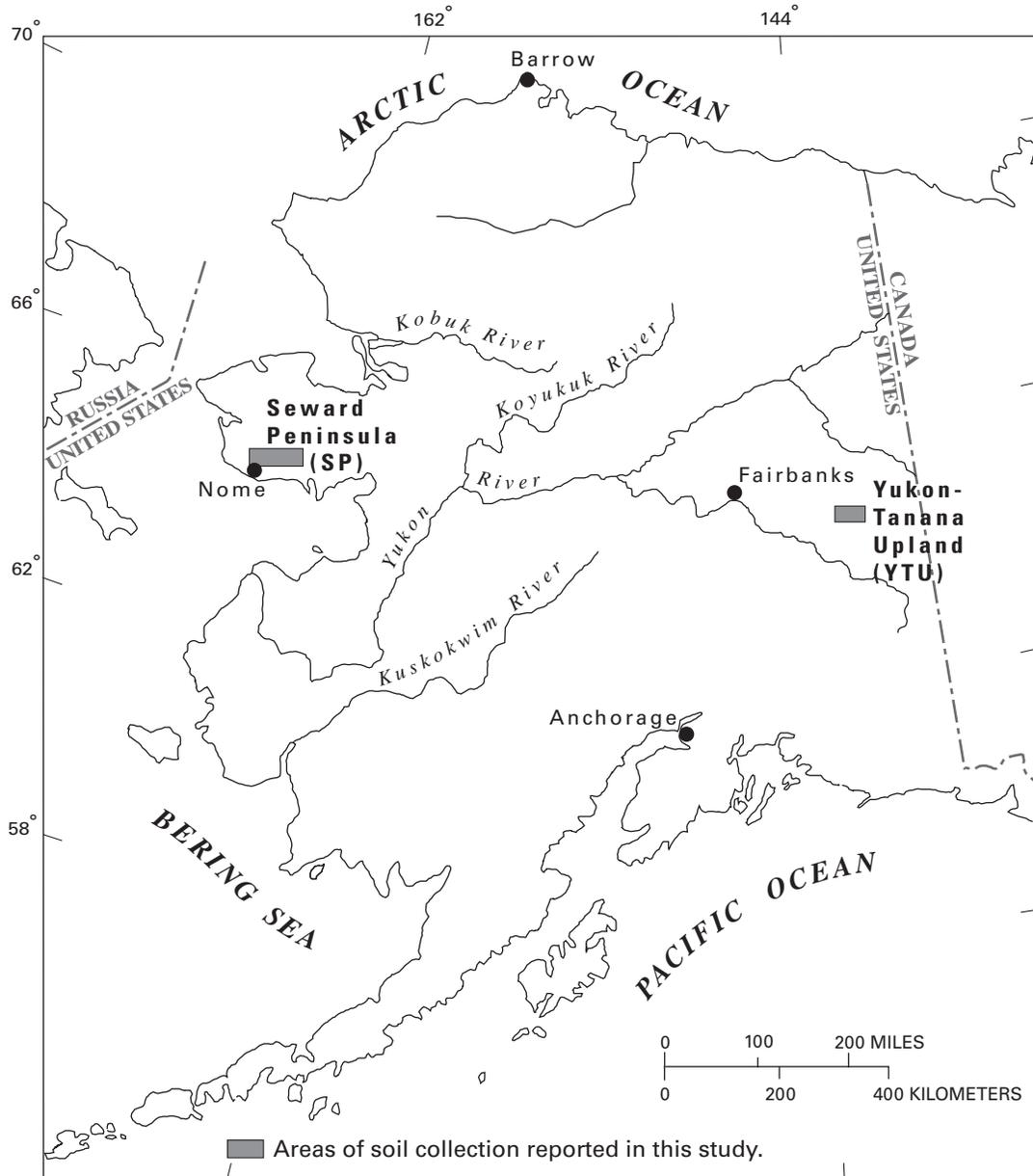


Figure 1. Location of the soil sampling areas in the Yukon-Tanana Upland (YTU) and the Seward Peninsula (SP), Alaska.

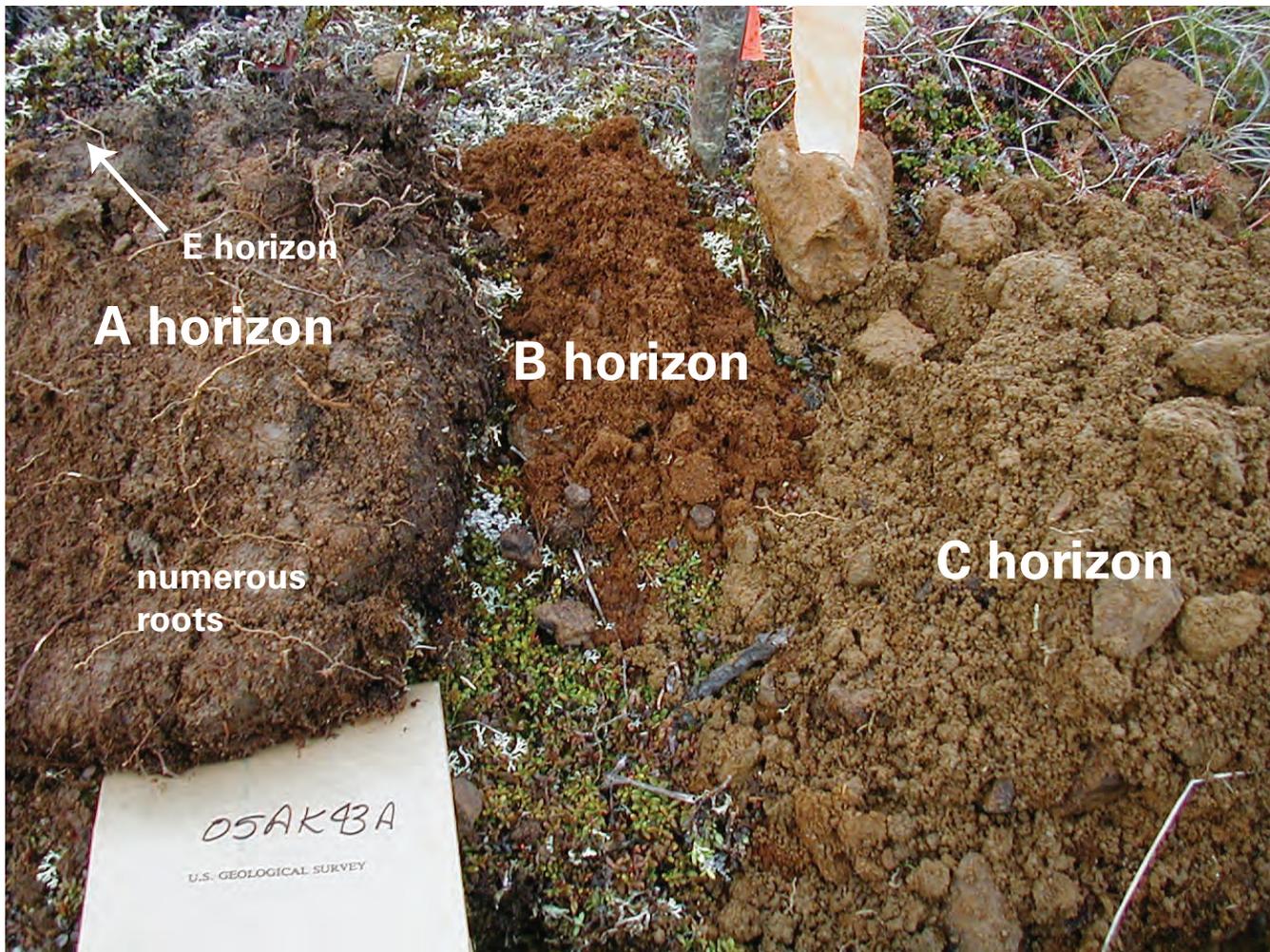


Figure 2. Typical well-drained boreal forest Inceptisol developed over granite. The A horizon, held together by numerous plant roots, is overturned in this photograph to show its dark-brown color and the presence of a weak, ash-colored E horizon.

Geology

The oldest geologic units within YTU are composed of a series of biotite-sillimanite gneiss, quartzofeldspathic biotite gneiss, and a sequence of metagraywacke that is locally inter-layered with quartzite and metapelite. The protoliths for these metasedimentary units included epiclastic to pelitic sediments. The region experienced two major episodes of plutonism, one during the Devonian (~365 million years before present, Ma) and another during the Cretaceous (~104–113 Ma). In addition to soils developed over the metasediments, some of the soils we collected in YTU were developed over the plutonic/intrusive rocks and included the Goodpaster granite, the Swede Peak granite, granodioritic dikes, and various granodioritic to granite stocks. For a thorough discussion of the geologic setting, deformational history, and age of mineralization for the YTU area, see Wilson and others (1985), Dusel-Bacon and Hansen (1992), Dusel-Bacon and others (2002), Dilworth and others (2002), Selby and others (2002), Day and others (2003), and Day and O'Neill (in press).

Like the YTU, the Seward Peninsula (SP) study area (fig. 1) is predominantly a crystalline terrane. Our sites were located exclusively over metasedimentary bedrock of the Nome Group (Proterozoic to Paleozoic age) that has been subjected to blueschist-facies metamorphism (Werdon and others, 2005). Unlike YTU, however, the Nome Group rocks are composed of interlayered metasedimentary and igneous rocks, including chlorite-rich schist, mafic granofels, marble, impure marble quartzite, and metagraywacke (Bundtzen and others, 1994; Till and others, 1986; Till and Dumoulin, 1994; Werdon and others, 2005). The soils developed over the Nome Group rocks are of particular interest, as the schist can contain as much as 5 percent graphite and the quartzite 2 to 10 percent (Werdon and others, 2005). It is suspected that bedrock areas with high graphite content could also be high in total cadmium (John F. Slack, U.S. Geological Survey, personal commun., 2004). In previous work, we became curious about the mobility and bioavailability of cadmium in these soils (Gough and others, 2001) and its bioaccumulation by willow (Gough and others, 2002).

Methods

Soil samples were collected over crystalline (metamorphic and intrusive) bedrock between 1999 and 2005 from throughout the Big Delta B-1 and B-2 quadrangles of the YTU (Gough and others, 2005). In 2004 and 2005 we collected soils developed over metasediments (schist and quartzite) on the SP. An effort was always made to collect mature, residual soils whenever possible. The presence of loess in the YTU soils was ubiquitous but variable; in SP soils the presence of loess was ubiquitous and uniformly less in volume than in the YTU soils. Sites were located well above contemporary flood levels on slopes that did not exceed a 15 percent grade. Cryoturbated soils were observed but these sites were purposely avoided; most commonly they were demonstrated by the mixing of soil horizon boundaries and by the presence of frost boils at the surface.

Soil study sites were selected on the basis of the following landscape and soil criteria: (1) soils developed over known lithologic units were targeted, (2) peaty soils were avoided, (3) permafrost where present was at a depth >30 cm, and (4) soils were mature, having recognizable soil-horizon development. Sites were also selected on the basis of the following ecosystem criteria: (1) sites were in boreal forests and in open tundra or shrub-tundra, (2) sites were selected that had not been recently burned (within the past 30–50 years based on tree-ring examination), and (3) sites were as well drained as possible for the area (usually with a southerly or ridge crest exposure). Commonly the sites were well drained if they lacked permafrost.

At least one soil pit was dug at each study site. Where available, samples of A1, B, and C soil horizon material (about 1 kilogram (kg) of each) were collected using a spade, mixed separately using a plastic spatula and bucket, placed in paper U.S. Geological Survey (USGS) soil sample bags, and stored at room temperature. In the laboratory the soils were dried (ambient temperature, forced air), mechanically disaggregated, and sieved to pass 10 mesh (2 millimeters, mm), and the <10-mesh material was further ground to pass a 100-mesh sieve (150 micrometers, μm). The ground material was digested and subjected to chemical analyses to determine elemental content (table 1).

Table 1. Analytical methodology for parameters reported for soils, soil leachate, and rocks. The methods follow those detailed in Crock and others (1999), Taggart (2002), and Eberl (2003; 2004).

Parameter	Method
Element concentrations	Inductively coupled plasma-mass spectrometry (ICP-MS)
Ash yield of soil	Gravimetric
Quantitative bulk mineralogy of soil	Powder X-ray diffraction using RockJock computer program (Eberl, 2003)

Sequential partial extraction of soils used 1 gram (g) of bulk soil material sieved to <2 mm and 25 milliliters (mL) of

extraction solution for each of six treatments (fractions). A modification of the methods of Hall and others (1996a; 1996b) and Chao (1984) was used as follows: Fraction I—(1 molar (*M*) sodium acetate), target: easily exchangeable and carbonate-sorbed mineral phases. Fraction II—(0.1*M* sodium phosphate brought to pH 10 using nitric acid), target: labile component associated with organic matter. Fraction III—(0.25 *M* hydroxylamine hydrochloride in 0.25 normal (*N*) HCl), target: amorphous Fe- and Mn-oxides. Fraction IV—(1 *M* hydroxylamine hydrochloride in 25 percent acetic acid), target: crystalline Fe-, Mn-, and Al-oxides, secondary sulfides, monosulfides, plus the edges of some silicate minerals. Fraction V—(1 g potassium chlorate and 10 mL HCl), target: sulfide minerals. Fraction VI—(four-acid “total” dissolution of residue (HF, HCl, HClO₄ and HNO₃)), target: silicate and some resistate minerals.

Quantitative bulk soil mineralogy was determined by powder X-ray diffraction analysis for a selected subset of unground samples of the A, B, and C horizon soils from both study areas. For details of this method, using the RockJock computer program coupled with a Cu-K α radiation diffractometer, see Eberl (2003; 2004).

Table 1 lists the laboratory methodologies used in the analysis of rocks, soils, and soil leachate samples. The complete geochemistry of area bedrock associated with the YTU soils is found in Gough and others (2005) and in Day and O'Neill (in press). Details of the quality assurance-quality control protocols of the Denver laboratories of the USGS are given in Crock and others (1999) and Taggart (2002). These methods incorporate the periodic analysis of blanks, laboratory-made duplicates, and several USGS and National Institute of Standards and Technology (NIST) standard reference materials for quality control purposes.

Results and Discussion

Soil Weathering — Major Element Ratios

Muhs and others (2004) used selected major element ratios (mobile-to-immobile elements) as a proxy for examining mineral depletions due to chemical weathering in soils from south-central Alaska. They examined CaO/TiO₂ (plagioclase and hornblende), K₂O/TiO₂ (mica and potassium feldspar), and Fe₂O₃/TiO₂ (“podzolization,” or downward migration of organic matter, Fe, and Al), reasoning that a loss of these mobile oxides in surface soil horizons could demonstrate weathering. Figure 3A shows the percentile box plots for the ratio of these major oxides in A, B, and C horizon soils. The plots are segregated by ecosystem (soils developed in boreal forests and tundra) and by bedrock type (crystalline: metamorphic and intrusive (YTU), and metasediments: schist and quartzite (SP)). Of the 52 soil profiles that these data represent, 45 were developed over metamorphic and intrusive bedrock (YTU) and 7 were over schist and quartzite (SP). Two of the soil profiles from YTU lacked a recognizable B horizon.

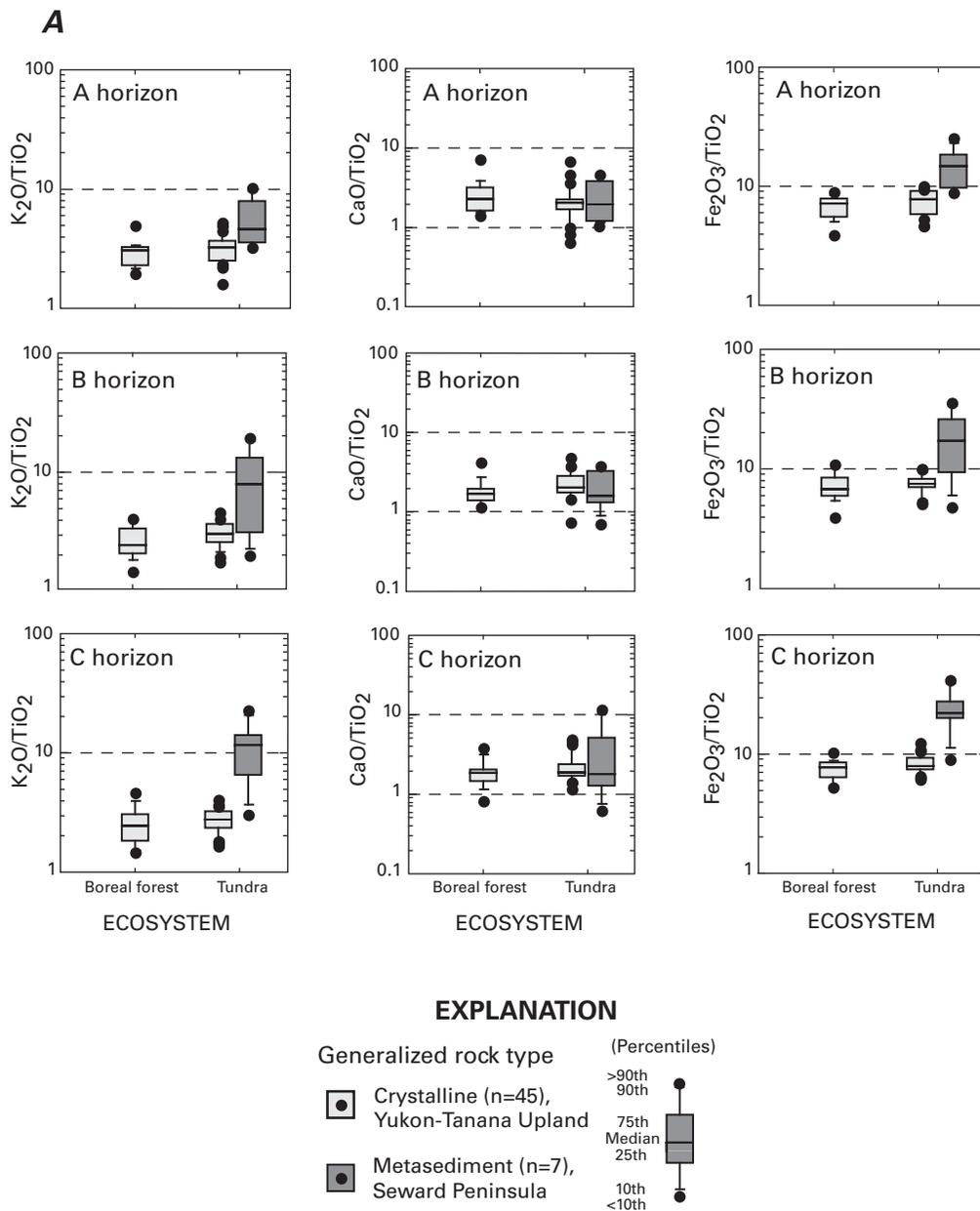


Figure 3A. Box plots of the ratios of K_2O/TiO_2 , CaO/TiO_2 , and Fe_2O_3/TiO_2 from soils (three horizons) developed over two generalized rock types in boreal forest and tundra ecosystems. Soils developed over crystalline rocks are from the Yukon-Tanana Upland, whereas soils developed over metasediments are from the Seward Peninsula, Alaska (table 2).

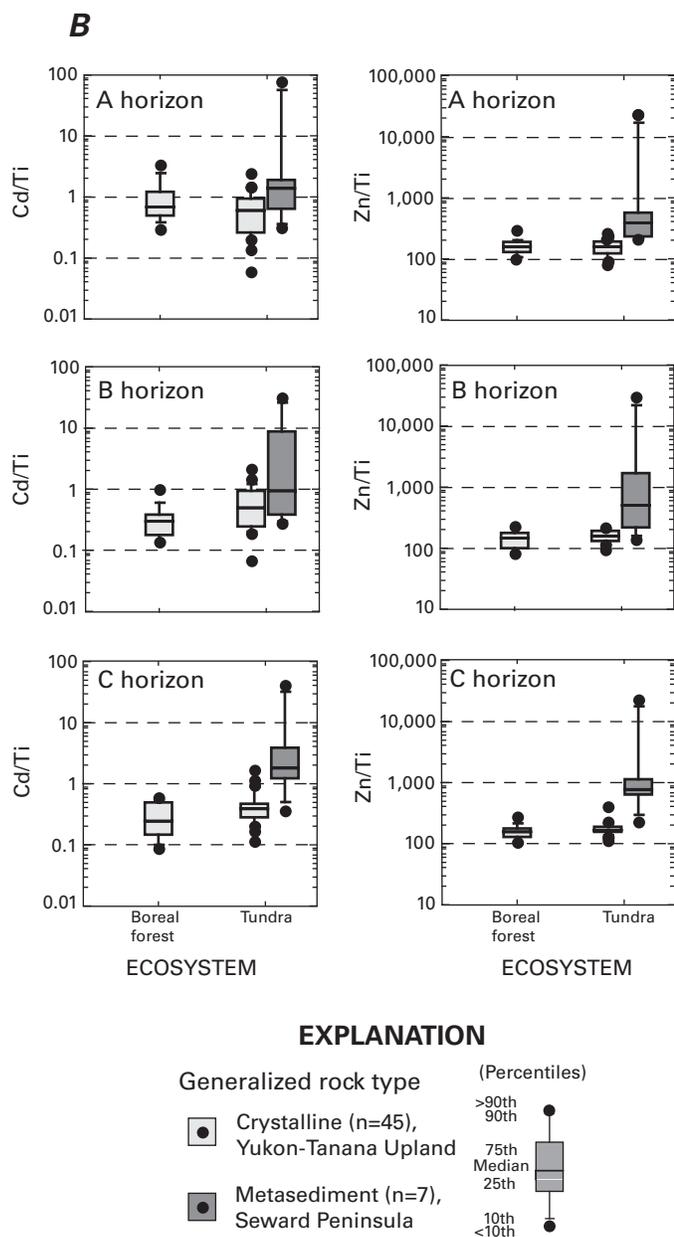


Figure 3B. Box plots of the ratios of Cd/Ti and Zn/Ti from soils (three horizons) developed over two bedrock types in boreal forest and tundra ecosystems. Soils developed over crystalline rocks are from the Yukon-Tanana Upland, whereas soils developed over metasedimentary rocks are from the Seward Peninsula, Alaska (table 2).

If one assumes that time is nearly the same for the development of these soils, figure 3A shows that very little difference exists, between the two ecosystems tested, in the median or variance for ratios of CaO/TiO_2 , $\text{K}_2\text{O}/\text{TiO}_2$, or $\text{Fe}_2\text{O}_3/\text{TiO}_2$.

The ratios for $\text{K}_2\text{O}/\text{TiO}_2$ and $\text{Fe}_2\text{O}_3/\text{TiO}_2$ are generally greater, however, in soils developed over SP schist and quartzite compared to soils from YTU. In addition, the ratios for $\text{K}_2\text{O}/\text{TiO}_2$ and possibly $\text{Fe}_2\text{O}_3/\text{TiO}_2$ show a slight loss in the A horizon, compared to samples at greater depth (especially for soils over schist and quartzite). This could be interpreted as demonstrating the downward migration of these oxides in soils over this bedrock type. As stated above, we do not have control over time (of soil development) and this presents some uncertainty to the comparison of geochemical signatures.

Figure 3B presents plots for total cadmium (Cd) and zinc (Zn) normalized to total titanium (Ti) in the A, B, and C horizon of soils developed in the same two ecosystems as above. Although, in general, the geochemistry of Cd and Zn in soils is similar, Cd and Zn behave differently in the soils of this study. Some loss in Cd with depth is seen for YTU soils in the boreal forest environment. Little change in Cd is noted with depth in the tundra soils. Zinc shows little or no change with depth among bedrock types or among ecosystems. The trends for Cd are related in part to the biogenic cycling of Cd (Gough and others, 2001; Gough and others, 2002) and its probable association with organic matter (McArthur and others, 2001). Cadmium is bioavailable in this environment and is being absorbed by plants, taken up into leaf tissue (especially willows), and then redeposited on the soil surface through leaf drop. Zinc does not demonstrate this type of biogenically mediated enrichment.

Soil Weathering — Soil Bulk Mineralogy

The degree of chemical weathering of these soils can also be examined through the analysis of the relative abundance of primary and secondary minerals among soil horizons. Nine soil samples (three sites each with three horizons) in both YTU and SP were examined quantitatively for their bulk mineralogy using powder X-ray diffraction (table 2).

There are major differences in the non-clay mineralogy of the soils from the two study areas with quartz as the most abundant non-clay mineral followed by peat (“mineral” peat as defined by X-ray diffraction) > plagioclase feldspar > goethite (table 2). These four primary minerals make up ~60 weight percent of the bulk mineralogy in the YTU soils and ~50 weight percent in the SP soils. Both quartz and peat are about twice as abundant in the YTU soils, compared to the SP soils. Table 2 shows the dramatic and rapid decrease in peat with soil depth in the YTU soils; this pattern is not so pronounced in the Arctic tundra SP soils. The quantitative analysis of peat by X-ray diffraction correlates positively with total organic matter (as measured by loss on ignition) in a nearly 1:1 relation ($R^2 > 0.96$) for both area populations. Even after factoring out the influence of the dominant presence of quartz, a decreasing pattern of peat with depth is still not as dramatic for the SP soils (table 3).

Table 2. Bulk mineralogy (quantitative XRD) and site characteristics for tundra soils developed from bedrock and loess, Yukon-Tanana Upland and Seward Peninsula, Alaska.

[Crystalline (metamorphic and intrusive, YTU): Kgmh, Mount Harper granodiorite; Dag, Devonian augen gneiss; Metasediment (SP): OpCsq, Ordovician to Precambrian mixed unit of the Nome Group (graphitic schist and quartzite); OpCt, Precambrian mixed unit of the Nome Group (chlorite-rich schist and marble); --, mineral was not observed. Geologic units based on Weirton and others (2005)]

Sample identification	Soil horizon	Site elevation (meters)	Rock unit	Loss on ignition	Quartz	Potassium feldspar	Plagio-clase	Calcite	Dolo-mite	Amphi-bole	Weight Percent									
											Pyrite	Goethite	Apatite	Rutile	Peat	Total non-clay	2:1 clay	Chlorite	Muscovite	Total clay
Yukon-Tanana Upland (YTU)																				
05AK33A	A	1,150	Kgmh	21	20	4.1	15	--	--	0.2	0.3	--	0.2	24	64	16	9.4	11	36	
05AK33B	B			13	24	5.7	17	--	--	--	0.1	--	0.2	14	62	15	13	11	38	
05AK33C	C			8.0	32	6.2	18	--	--	.5	--	--	.2	8.3	66	16	11	6.9	34	
05AK35A	A	1,200	Kgmh	56	5.3	.7	3.9	--	--	--	.7	--	--	63	73	13	4.3	9.5	27	
05AK35B	B			13	27	7.6	21	--	--	--	.5	--	.5	14	71	17	8.8	3.4	29	
05AK35C	C			4.6	31	8.9	26	--	0.1	.7	--	--	.1	6.3	74	12	9.4	5.0	26	
Seward Peninsula (SP)																				
05AK37A	A	1,050	Dag	72	8.7	.9	4.9	--	--	--	.6	--	--	69	84	5.3	.5	9.9	16	
05AK37B	B			16	28	6.2	15	--	--	.2	--	--	.4	14	65	14	8.4	13	35	
05AK37C	C			6.9	27	4.5	18	--	--	1.2	.1	.3	--	14	65	15	10	10	35	
05AK011A	A	248	OpCt	8.8	39	.4	2.3	--	--	--	1.3	--	.1	9.8	53	1.6	3.7	41	47	
05AK011B	B			3.5	36	.8	1.5	--	.1	--	2.3	--	.6	3.5	45	2.2	5.3	48	55	
05AK011C	C			4.2	35	.4	1.3	--	--	--	3.7	--	.7	5.1	47	2.7	2.4	49	54	
05AK021A	A	233	OpCt	41	19	1.1	1.6	--	.2	--	.1	2.3	.2	39	64	5.5	.5	30	37	
05AK021B	B			3.5	44	2.5	2.1	0.2	--	--	3.2	.3	.1	6.2	59	2.4	4.7	34	41	
05AK021C	C			3.5	46	1.8	2.1	.2	--	--	3.7	.3	.1	6.5	61	3.0	4.0	32	39	
05AK131A	A	128	OpCsq	10	45	1.6	2.1	--	--	--	2.4	--	.2	17	68	5.9	9.1	17	32	
05AK131B	B			8.8	47	2.0	2.2	--	--	--	.1	2.3	.1	13	66	10	9.4	14	34	
05AK131C	C			8.8	48	1.8	2.2	--	--	--	2.5	.2	--	12	67	6.5	13	15	34	

Table 3. Ratio of quartz to major soil minerals (calculated on a weight percent basis) in A, B, and C horizon soil samples from three sites in the Yukon-Tanana Upland (YTU) and three sites in the Seward Peninsula (SP).

Sample identification	Potassium feldspar	Plagioclase feldspar	Goethite	Peat	Total non-clay minerals	2:1 clay	Chlorite	Muscovite	Total clay minerals
Crystalline bedrock (YTU)									
05AK33A	4.80	1.30	65.7	0.81	0.31	1.25	2.10	1.82	0.55
05AK33B	4.28	1.46	61.0	1.72	.40	1.61	1.94	2.32	.64
05AK33C	5.16	1.75	64.0	3.86	.49	2.00	2.86	4.64	.94
05AK35A	7.57	1.36	7.57	.08	.07	.41	1.23	.56	.20
05AK35B	3.55	1.29	54.0	1.93	.38	1.57	3.07	7.94	.92
05AK35C	3.51	1.20	156	4.95	.42	2.60	3.32	6.24	1.18
05AK37A	9.67	1.78	14.5	.13	.10	1.64	17.4	.88	.55
05AK37B	4.53	1.87	35.1	1.98	.43	2.01	3.35	2.20	.80
05AK37C	5.96	1.49	89.3	1.94	.41	1.76	2.65	2.68	.76
Metasediment bedrock (SP)									
05AK011A	97.3	16.9	29.9	3.97	.73	24.3	10.5	.94	.83
05AK011B	44.5	23.7	15.5	10.2	.79	16.2	6.72	.75	.65
05AK011C	88.3	27.2	9.54	6.92	.76	13.1	14.7	.73	.66
05AK021A	16.8	11.6	8.04	.47	.29	3.36	37.0	.61	.51
05AK021B	17.8	21.1	13.9	7.16	.75	18.5	9.45	1.32	1.09
05AK021C	25.5	21.9	12.4	7.06	.76	15.3	11.5	1.43	1.17
05AK131A	28.4	21.6	18.9	2.72	.66	7.69	4.99	2.73	1.44
05AK131B	23.6	21.4	20.5	3.77	.71	4.71	5.01	3.27	1.39
05AK131C	26.5	21.7	19.1	3.94	.72	7.34	3.82	3.29	1.42

Plagioclase feldspar and potassium feldspar show an increase with increasing soil depth in the YTU soils but not in the SP soils (table 2); however, the ratio of quartz to feldspar remains fairly constant with depth for both areas (table 3). Because the relative amount of plagioclase remains the same with depth, we cannot say that demonstrable feldspar weathering is occurring in these soils. This is in contrast to the findings of Legros (1992), who reports that feldspars in podzolized soils of the subalpine region of the Alps dissolved relatively quickly (tens of years) with calcic plagioclases less stable than sodic, which are less stable than potassic feldspar.

Our soils, however, are greatly influenced by the presence of loess (YTU more so than SP), and the ratio of quartz to muscovite does not change radically with soil depth (table 3). This uniformity means that the ratios are independent of soil horizon and therefore of weathering intensity (Evans, 1992). The age, source, and weathering of loess versus bedrock, and of their relative importance to soil geochemistry, need further study.

The clay minerals in these soils are distinctive between the two areas (table 2). Soils in the YTU, derived from the weathering of metamorphic and intrusive bedrock, possessed an abundance of 2:1 clays (smectite and illite) and muscovite (together ~20 weight percent). In contrast, the SP soils, developed over schist and quartzite, were dominated by muscovite (40 weight percent) with lesser amounts of 2:1 clay and chlorite. The amount of muscovite in these latter soils is indeed large and may represent either a source of layered silicates or, more probably, a much-reduced rate of soil weathering (Nagy, 1995). Little variability with depth is noted for the clay minerals for either area (table 2); however, table 3 shows that the YTU soils have less muscovite (and total clay) relative to quartz with depth. The abundance and distribution of clay minerals indicates that some clay formation is occurring in the upper horizons of the YTU soils; there is no indication that this is occurring in the SP soils.

The simple regression between muscovite, total clay, and loss on ignition (peat) (all in weight percent) to the concentration (parts per million, ppm) of Cd and Zn, in the nine soil samples (table 2) each from YTU and SP, is shown in figure 4. In general, the nine samples from YTU possess lower concentrations of both elements compared to the nine samples from the SP, and the values for the two areas comprise two distinct populations. Neither Cd nor Zn is significantly correlated with loss on ignition in either area (low R^2 values coupled with the disproportional influence of a few outlier sample points). Both Cd and Zn, however, are strongly and positively correlated with muscovite and total clay in the SP samples (fig. 4). These differences may be due to fluctuating redox potentials in these soils due to differences in seasonal saturation. This major difference in the concentration of Cd and Zn and in the relation

of Cd and Zn to muscovite and total clay between the two regions suggests different sources of the metals. The Zn/Cd ratios (around 250) suggest that, for the SP soils, the source of Cd and Zn is sphalerite in the loess.

In summary, these data show that although the nine samples from the three soil horizons from the YTU and from the SP represent similar ecosystems (herbaceous tundra), major differences exist between their bulk mineralogy due to geology, presence of loess, and the weathering (or lack thereof) of primary minerals. Little evidence exists for the weathering of feldspar or muscovite. In addition to geology, soil formation differences in these two areas are affected by differences in climate, elevation, and possibly time (table 2). These differences appear to affect the sequestration of Cd and Zn, with total clay and muscovite being important to these elements in soils from both areas. In this limited data set, twice as much peat was measured in the A and B horizons of the YTU samples, as in the SP samples whereas both areas have nearly equal amounts of total clay (table 2). SP soils, however, had very high values for the clay mineral muscovite. Soil sequential extraction was employed to further elucidate the mode of occurrence and potential bioavailability of Cd and Zn.

Chemistry of Soil Sequential Extraction Leachates

Figure 5 shows the results for Cd and Zn of the sequential extraction of 20 soil samples from 7 YTU soil profiles. Descriptions of the soils used in figure 5 are given in table 4. Three of the seven profiles were well-drained silty Inceptisols developed over granodiorite bedrock, whereas four of the seven were poorly drained silty Gelisols developed over both granodiorite and augen gneiss. In addition, five of the sites were within the tundra zone and one each in a floodplain and a boreal forest zone. The analytical scheme uses extractants that increase in the severity with which they attack soil exchange sites and mineral structure (table 5). Such schemes provide a gradient for the physicochemical association strength between elements and solid phases (Chao, 1984). Element solubility in such schemes can be related to availability and mobility in the environment.

Considerable differences in the proportion of Cd and Zn associated with the various extraction leachates is seen in the plots (fig. 5). Differences, although not necessarily major, are also evident among the three soil horizons. Most of the Cd (>50 percent) is easily to conditionally available and is associated with the I, II, and III fractions. Differences among the soil horizons are especially evident when comparing the Cd associated with these same fractions in all seven soil profiles shown.

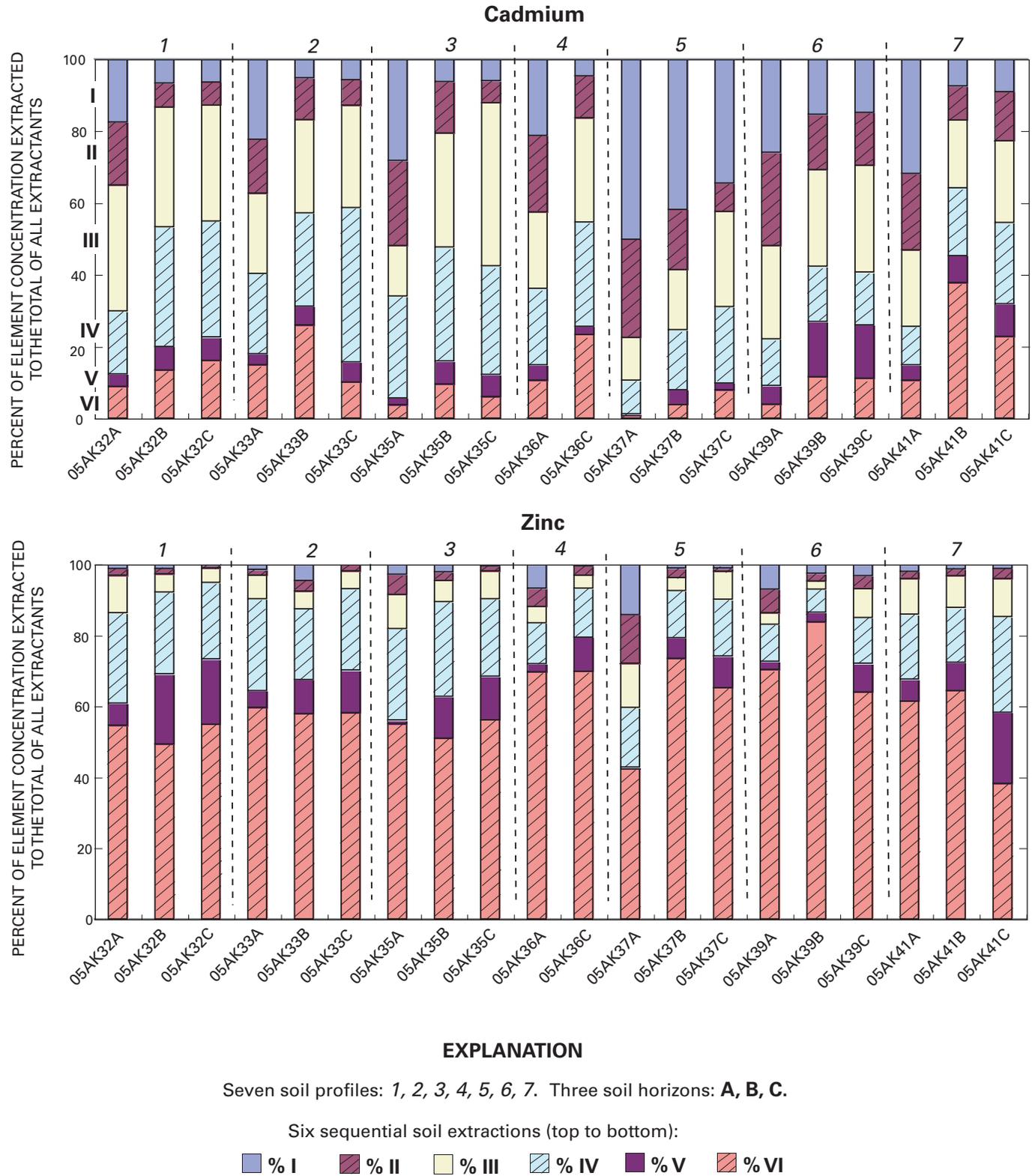


Figure 5. Results of the sequential extraction for cadmium and zinc of three soil horizons (A, B, and C) using seven different soil profiles and six extractants (see text for explanation and table 4 for soil sample descriptions). All samples are from the Yukon-Tanana Upland.

Table 4. Yukon-Tanana Upland soil samples used in the sequential extraction results shown in figure 5.

Sample identification	Soil horizons	Soil classification	Location		Elevation (meters)	Ecosystem	Geology
			Latitude	Longitude			
05AK32	A, B, C	Inceptisol	64.3392	-144.2573	1,050	Tundra	Granodiorite
05AK33	A, B, C	Inceptisol	64.3394	-144.2506	1,150	Tundra	Granodiorite
05AK35	A, B, C	Inceptisol	64.3435	-144.2517	1,200	Tundra	Granodiorite
05AK36	A, C	Gelisol	64.2903	-144.2537	1,030	Floodplain	Granodiorite
05AK37	A, B, C	Gelisol	64.2913	-144.2603	1,050	Tundra	Augen gneiss
05AK39	A, B, C	Gelisol	64.3620	-144.2915	1,120	Tundra	Augen gneiss
05AK41	A, B, C	Gelisol	64.4428	-144.2750	675	Boreal Forest	Granodiorite

Table 5. Chemistry and targeted soil fraction of six (I-VI) sequential extractants of soil samples from the Yukon-Tanana Upland, Alaska. (Extractions performed using modifications of the method of Hall (1996a; 1996b) and Chao (1984).)

M, molar; *N*, normal; g, gram; mL, milliliter]

Extractant	Chemistry	Targeted soil fraction
I	1 <i>M</i> sodium acetate (pH 5)	Easily exchangeable component (adsorbed as well as carbonate)
II	0.1 <i>M</i> sodium phosphate (pH 10)	Labile organic component
III	0.25 <i>M</i> hydroxylamine hydrochloride and 0.25 <i>N</i> hydrochloric acid	Amorphous Fe- and Mn-oxide and some amorphous Al-oxide component
IV	1 <i>M</i> hydroxylamine hydrochloride and 25 percent acetic acid	Crystalline Fe-oxide; monosulfide and secondary sulfide component
V	1 g potassium chlorate and 10 mL hydrochloric acid	Sulfur-bound component
VI	Four-acid digestion (hydrofluoric, hydrochloric, perchloric, and nitric)	Total residual component

Total Cd concentrations in the seven soil profiles used in the sequential soil extraction analysis had median values of 0.12, 0.07, and 0.07 ppm for the A, B, and C horizons, respectively, and median Zn values of 56, 71, and 80 ppm. None of the bedrock types over which these soils developed had measurable Cd (all <1.0 ppm¹); median Zn concentrations¹ were as follows: granitoids, 35 ppm; metasediments, 94 ppm; diorite-tonalite, 79 ppm; augen gneiss, 52 ppm (Gough and others, 2005).

Cadmium, associated with the I, II, III, and IV soil extraction fractions (easily exchangeable, organic, amorphous and crystalline Fe-, Mn-, and Al-oxides/hydroxides) is fairly evenly divided among these four fractions and follows a general decreasing trend with depth (A-C horizons; fig. 5). In addition, a majority of the soil Cd is tied up in these four fractions, with commonly <25 percent associated within the

IV and V fractions combined. Except for possibly sample 05AK37 (soils developed over augen gneiss), no meaningful differences are observed in figure 5 in the distribution of Cd or Zn among the sequential extraction fractions for the two bedrock types examined. Unlike Cd, a majority of the Zn is tied up in primary soil minerals (fractions V and VI); in a majority of the soil profiles, <20 percent of the Zn appears to be readily or conditionally bioavailable.

One additional element of note is calcium (Ca). It is highly mobile in northern forests; however, a vast majority of the Ca pool is recycled and reused (Foth, 1990). In our sequential extraction study, Ca was found to be mostly associated with the I fraction (easily exchangeable as well as carbonate) and VI fraction (residual). The Ca in these soils that is bioavailable (mobile) generally follows the trend: A horizon > B horizon > C horizon. The ratio of CaO/TiO₂,

¹ Estimated crustal abundances of Cd and Zn are 0.11 and 75 ppm, respectively (Emsley, 1991).

discussed above for figure 3A, was also higher in the A horizon than deeper in the soil profile. Although the I fraction would release Ca from soil carbonates, these low pH soils (pH 3.8 – 6.3) have an abundance of both organic acids and carbonic acid in the A and B horizons that would affect carbonate dissolution. In addition, the bulk mineralogy for these soils (table 2) showed only fractions of a weight percent of calcite and dolomite. Further, we did not observe caliche in these soils. Van Cleve and others (1991) report that caliche can form (especially in interior Alaska floodplain soils) because of high summer temperatures that accompany low precipitation (300–400 millimeters per year, mm y^{-1}) and relatively high evapotranspiration ($>450 \text{ mm y}^{-1}$).

Soil Loess and Geochemical Signatures

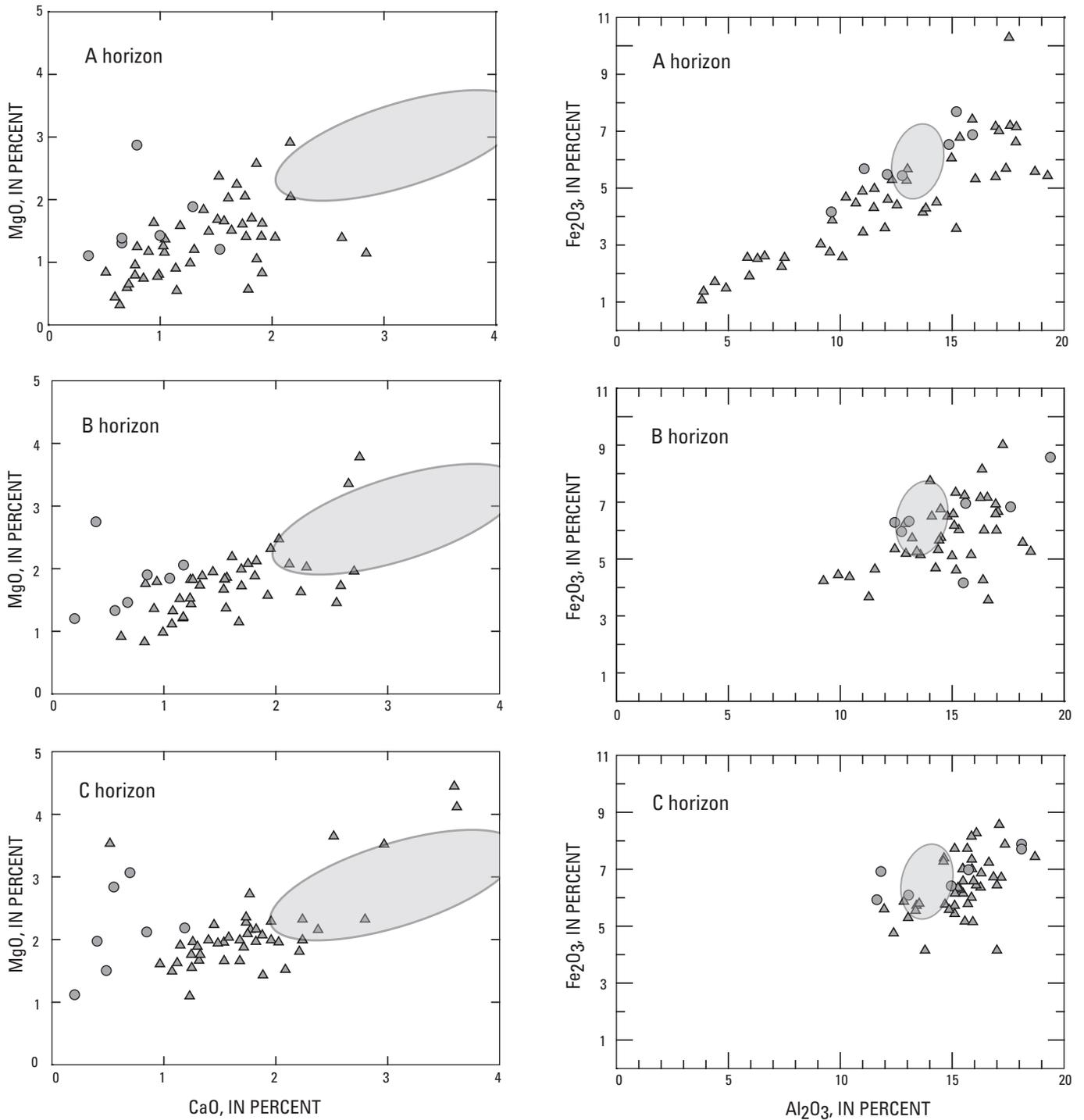
Soils of both the Yukon-Tanana Upland (YTU) and Seward Peninsula (SP) have a silty to silty-loam texture, especially in the A and B horizons. An important question is whether the silt fraction is predominantly eolian dust (Quaternary to Holocene, modern, or a mixture) or the result of in situ physical processes of rock shattering and cryoturbation. This distinction is important in the interpretation of soil geochemistry because loess deposition and soil weathering can be interpreted as competing processes (Muhs and others, 2004), and geochemical signatures related to bedrock thus are potentially confounded. These authors state that major loess deposition in central Alaska took place in the late Quaternary to Holocene ($<50 - 30$ thousand years ago, Ka) and that modern deposition

in the inland area of the YTU and SP, sampled in this study, is now occurring at very low rates.

The samples in this study were not geochemically analyzed on the basis of particle size fractionation, so geochemical data on just the silt-sized portion are not available. Instead, the soils were sieved to <10 mesh and then ground to <100 mesh prior to analysis.

Figure 6 presents plots of CaO versus MgO and Al_2O_3 versus Fe_2O_3 in soils developed over both the YTU and SP bedrock types. The correlation between CaO and MgO is poor, which is expected in soils low in carbonate and developed from metamorphic and intrusive rocks (YTU) and from metasedimentary rocks (SP). In addition, the two bedrock types (metamorphic and intrusive and metasediments) are moderately well segregated in plots based on CaO and MgO (fig. 6).

A linear correlation exists between Al_2O_3 and Fe_2O_3 in the A horizon for both bedrock types; this relation is not present in the B and C horizon soils. This correlation implies that Fe and Al are coupled in the upper soil horizon and is reflective of the presence of oxides and (or) hydroxides. As discussed above, Cd is one element closely associated with soil oxides and (or) hydroxides. The absence of any correlation between our plots of CaO and MgO and of Al_2O_3 and Fe_2O_3 with the geochemical signatures reported by Muhs and others (2003b) for central Alaskan late Quaternary loess (shown by the shaded ovals in fig. 6) suggests that the silty material in our soils is probably more locally derived dust as well as the product of in-place bedrock shattering.



EXPLANATION

- | | | |
|-----------------------|---|---|
| Generalized rock type | | |
| ▲ | Crystalline (n=45) | |
| ● | Metasediment (n=7) | |
| | Central Alaskan |  |
| | Loess Signature | |
| | (estimated from Muhs and others, 2003b) | |

Figure 6. Plots of CaO versus MgO and Al₂O₃ versus Fe₂O₃ in three soil horizons segregated by bedrock type. Also plotted are the values for central Alaska loess of late Quaternary age (estimated from Muhs and others, 2003b). n, number of samples.

Summary

Studies of silty textured soils developed over crystalline bedrock terrane (metamorphic and intrusive from the Yukon-Tanana Upland and schist and quartzite from the Seward Peninsula) were examined for their differences in chemical weathering and for possible landscape geochemical patterns. Chemical weathering signature differences were also examined on the basis of the ecosystem within which the soils developed (boreal forest and tundra).

There are major differences in the nonclay and clay mineralogy of the soils from the two study areas. Of the nonclay minerals, quartz was the most abundant followed by peat ("mineral") > plagioclase feldspar > goethite. The absolute amount of plagioclase and potassium feldspar increases with increasing depth in the YTU soils, but the relative amount of feldspar to quartz does not. This trend would suggest, therefore, that very little weathering of feldspar is occurring in these soils. Of the clay minerals, soils in the YTU, developed over metamorphic and intrusive bedrock, possessed an abundance of 2:1 clays and muscovite, whereas the SP soils, developed over metasediments, were dominated by muscovite with lesser amounts of 2:1 clay and chlorite. In the YTU soils, the relative amount of total clay to quartz did decrease with soil depth (more clays in the upper soil horizons), which also suggests little weathering in these soils.

Examination of the ratio of mobile (K_2O , CaO , and Fe_2O_3) to immobile (TiO_2) major oxides showed that very little difference exists in the chemical weathering of soils developed among the ecosystems tested (hypothesis 2). This means that in the short-term, changes in weathering signatures due to climate change may be too subtle to be easily detected using these methods. Differences were observed among the bedrock types, especially when comparing soils developed over schist and quartzite with soils developed over metamorphic and intrusive bedrock. We assume that the age of these soils is late Quaternary to Holocene; however, it is impossible to say for certain that geochemical differences are due exclusively to differences in bedrock geochemistry or to differences in weathering history.

A loss of Cd with soil depth is seen for soils developed over metamorphic and intrusive bedrock in the boreal forest. This trend is related to the mobility of Cd in these soils as well as to its biogenic cycling. Zinc does not display similar biogenically mediated trends and is less bioavailable than Cd. Sequential partial extraction results on these soils support this distinction between the relative bioavailability of Cd versus Zn.

Comparison of the relation between CaO and MgO and Al_2O_3 and Fe_2O_3 for A, B, and C horizon soils with values for late Quaternary loess from central Alaska (Muhs and others, 2003b) shows that the silty material in our soils does not match the loess signature and is most likely younger and more locally derived. Finally, major differences were

observed in the proportion of most elements among the A, B, and C horizon material sequestered in various soil fractions as measured by sequential soil extractions. These trends followed such variables as the decrease in organic matter, the change in clay minerals, and the change in the proportion of oxides and hydroxides with depth.

In this study we controlled the major factors that influence soil development except time. We assume that these soils are all approximately the same age, and their general uniformity in physical appearance, mineralogy, and chemistry lends support to this assumption. This uniformity underscores the slow nature of soil development in cold regions and the long periods of time that are required to affect observable changes. Should changes in the climate of the subarctic accelerate (specifically, permafrost melting and the attendant oxidation of trapped organic matter), changes in the mineralogical and geochemical soil development processes could also be expected to accelerate (Keller and others, 2007).

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