

Accepted Manuscript

Geological controls on soil parent material geochemistry along a northern Manitoba - North Dakota transect

R.A. Klassen

PII: S0883-2927(09)00120-6
DOI: [10.1016/j.apgeochem.2009.04.033](https://doi.org/10.1016/j.apgeochem.2009.04.033)
Reference: AG 2047

To appear in: *Applied Geochemistry*



Please cite this article as: Klassen, R.A., Geological controls on soil parent material geochemistry along a northern Manitoba - North Dakota transect, *Applied Geochemistry* (2009), doi: [10.1016/j.apgeochem.2009.04.033](https://doi.org/10.1016/j.apgeochem.2009.04.033)

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

**Geological controls on soil parent material geochemistry along a northern Manitoba
- North Dakota transect**

R. A. Klassen*

*Geological Survey of Canada, Department of Natural Resources, 601 Booth St., Ottawa,
ON, Canada K1A 0E8*

Email address: klassen@NRCan.gc.ca

Abstract

As a pilot study for mapping the geochemistry of North American soils, samples were collected along two continental transects extending east-west from Virginia to California, and north-south from northern Manitoba to the U.S.- Mexican border and subjected to geochemical and mineralogical analyses. For the northern Manitoba – North Dakota segment of the north-south transect, X-ray diffraction analysis and bivariate relations indicate that geochemical properties of soil parent materials may be interpreted in terms of minerals derived from Shield and clastic sedimentary bedrock, and carbonate sedimentary bedrock terranes. The elements Cu, Zn, Ni, Cr and Ti occur primarily in silicate minerals decomposed by aqua regia, likely phyllosilicates, that preferentially concentrate in clay-sized fractions; Cr and Ti also occur in minerals decomposed only by stronger acid. Physical glacial processes affecting the distribution and concentration of carbonate minerals are significant controls on the variation of trace metal background concentrations.

1. Introduction

Regional soil geochemical surveys are increasingly carried out to support better decision-making for environmental and human health protection (e.g., Shacklette and Boerngen, 1984; McGrath and Loveland, 1992; Reimann et al., 1998, 2003; Salminen et al., 2005). The interpretation of geochemical background variation in soils is ultimately based on knowledge of the geological origins of soil parent materials and their variation. In addition to geochemical properties, the mineralogy of soil parent materials determines a wide range of environmental properties, including soil weathering effects, element speciation, fertility, structure, water retention, and buffering capacity. Hence, understanding geological variability, expressed by provenance, process and past, is critical to the interpretation of geochemical background variation and the application of geochemical data in societal decision-making. Provenance refers to the geological origins

of soil parent materials, process refers to the geological actions of wind, water, ice, and gravity acting at the earth's surface, and past to the stratigraphic record of change in process over time.

As a pilot study for mapping the geochemistry of North American soils (the North American Soil Geochemical Landscapes Project), two continental-scale transects were sampled in 2004 by personnel of the United States Geological Survey and the Geological Survey of Canada (Smith et al., 2005, 2009) (Fig. 1). The transects extend east-to-west from Virginia to California, and north-to-south from northern Manitoba to the U.S.-Mexican border. In addition to illustrating regional variations due to climate and vegetation, geochemical profiles along the transect may be interpreted in terms of bedrock and surficial geological terranes, the effects of geological process, and the stratigraphic record (e.g. Shilts, 1978, 1984). Here, geological controls on the geochemical properties of soil parent materials for the Manitoba - North Dakota segment of the north-south transect are examined with emphasis on geological factors affecting the distributions and concentrations of major elements and selected trace elements (Cu, Ni, Cr, Zn and Cd) associated with environmental and human health risk.

2. Area descriptions

2.1 Bedrock geology

The soil sampling transect for this study (Fig. 1) extends ~1000 km from near Leaf Rapids in northern Manitoba (Latitude 57°N) to northern North Dakota (Latitude 48°N). It crosses 3 distinct bedrock terranes, including the Precambrian Shield in the north, the Paleozoic Platform in the central Interlake Region, and the Western Canada Sedimentary Basin (WCSB) in the south. The Shield terrain is compositionally complex, comprising igneous, metasedimentary and metavolcanic bedrock. The Platform is composed predominantly of limestone and dolostone bedrock, with sandstone and shale of the Winnipeg and Red River formations stratigraphically lowest. The WCSB comprises Mesozoic-age clastic sedimentary rock, including sandstone, siltstone and black shale.

2.2 Surficial geology

From north to south, overburden comprises glaciolacustrine sediment; till and minor glaciofluvial sediment in the Interlake region; glaciolacustrine sediment south of Lake Manitoba; and an assemblage of glacial, glaciofluvial, and glaciolacustrine sediments in North Dakota (not shown) (Fig. 2). Across Manitoba, former ice flow directions range from southwestward to southeastward. Near Grand Rapids in the northern Interlake region, the transect crosses a major moraine, the Pas Moraine. In southeastern Manitoba, 5 tills are distinguished by heavy mineralogy, carbonate mineral content and texture (Teller and Fenton, 1980). In the Interlake Region, two tills are distinguished, with the uppermost relatively carbonate-rich (Thorleifson et al., 1994). In North Dakota, glacial drift comprises 20-30% Shield-derived and 10-35% Platform-derived detritus, with the remainder derived from WCSB bedrock (Moran et al., 1976, Table 4). Glacial lake sediments are largely silt and clay, with the southern deposits coarser-grained than the northern as the result of deltaic sedimentation from eastward-flowing rivers and nearshore reworking during glacial lake emergence.

3. Methods

Based on the site selection protocol proposed for the continental mapping project (Garrett, 2009), samples were collected along the transect at 24 locations spaced at approximately 40-km intervals, with field duplicates collected at 6 additional sites (Figs 1, 2). Although, for logistical reasons, sampling was near (~50 m) rural roads, the soil parent material types sampled and the physiographic settings are considered to be representative of their surrounding area.

At each site, samples of O-, A- and C-soil horizons were collected for the pilot study soil survey (Smith et al., 2005, 2009). For this study, a sample of the least weathered overburden that could be obtained by soil auger was also collected. The samples are representative of the soil C horizon, having been collected at depths of 50 – 80 cm and below the soil B horizon identified through secondary Fe oxidation colours. These samples are considered to represent a reasonable approximation of the geochemistry and mineralogy of the soil parent material at each site. Prior to placing in plastic sample bags, soil in contact with the metal auger was discarded to avoid contamination. At 4 sites where distinct sediment facies were observed, a second sample was collected to estimate

site geochemical variability. In southern Manitoba, a Cretaceous black shale sample was also collected for analysis because that bedrock unit is known to be Cd-rich.

Geochemical and mineralogical properties are based on analysis of the silt- and clay-sized (<0.063 mm) and the clay-sized (<0.002 mm) fractions. Although finer than the <2-mm fraction of soil commonly used in environmental studies, the fractions were chosen to minimize geochemical variation due to textural variation both at and between sites, and to focus on size fractions that are typically trace-element rich and potentially most environmentally reactive (Shilts, 1995, 1996). The silt and clay-sized fraction was obtained by sieving samples air-dried at low temperature (30 °C). The clay-sized fraction (<0.002 mm) was separated by wet centrifuge methods (Lindsay and Shilts, 1995). The soft Cretaceous shale sample was processed using the same methods after disaggregation using a ceramic mortar and pestle.

Mineralogical determinations are based on X-ray diffraction (XRD) patterns interpreted by personnel of the Mineralogy Laboratory, Geological Survey of Canada (GSC) using computer-aided pattern identification (JADE; Materials Data Inc.) (unpublished GSC report M05-3, 2005). For each sample, 3 sub-samples were mounted on glass slides and analyzed after air-drying, glycolation, and heat treatment (550 °C). The mineral analyses are semi-quantitative, with lower detection limits >3-5 wt%, and are non-specific for phyllosilicates, especially for mixed-layer minerals, which overlap in their XRD peak locations and are difficult to identify. For selected samples, XRD analyses of silt-sized minerals were qualitatively verified by examination of mineral grains using energy dispersive spectrometry coupled with scanning electron microscopy (EDS-SEM).

Geochemical analyses were provided by Activation Laboratories Ltd. Depending on the element, analytical results for the silt and clay-sized fraction are based on one or more of 4 protocols, including X-ray Fluorescence (XRF) after lithium metaborate fusion; inductively coupled plasma – atomic emission spectrometry (ICP – AES) after HF-HNO₃-HClO₄ (HCl leach) and after HCl – HNO₃ (aqua regia) acid digestions; and instrumental neutron activation analysis (INAA). The XRF and INAA results are total, the 3-acid digestion is near-total, and aqua regia digestion represents a partial dissolution of the sample. For most common rock-forming minerals, the 3-acid digestion is ‘total’,

although spinel (Cr) and zircon (Zr) are notable exceptions. Due to insufficiency of sample material, the clay-sized fraction was analyzed only after aqua regia digestion. Quality control is based on inclusion of 3 sample duplicates and one internal reference standard in each analytical batch of approximately 40 samples. Except for Cd, all elements occur in concentrations > 5-10x their lower detection limits, and analytical precision and accuracy are estimated to be $\pm 10\%$. For all analytical methods, the lower detection limit for Ba, Cu, Cr, Ni, Zn and Sr is 2 mg/kg.

For the silt- and clay-sized fraction, C was determined using a CO₂ infrared spectrometer after combustion in a LECO furnace. Total C is based on ignition at 1310 °C, and non-carbonate C at 550 °C ; carbonate C is estimated by subtraction of non-carbonate from total C determinations. Lower detection limits are 0.1 wt.% CO₂.

4. Results

Analytical results are linked to 4 transect segments distinguished by differences in dominant glacial sediment type (Fig. 2). From north to south, they are referred to as Northern Manitoba (North), Interlake Region, Southern Manitoba (South) and North Dakota. The North segment is associated with glaciolacustrine deposits. Although mostly underlain by crystalline, non-carbonate bedrock of the Canadian Shield, in its southernmost part it is underlain by Paleozoic carbonate bedrock. The Interlake segment is dominated by till, although glaciolacustrine and glaciofluvial sediment occur at two sites, and it is underlain by Paleozoic carbonate bedrock. The South segment is characterized by glaciolacustrine deposits, and the North Dakota segment by undifferentiated glacial deposits, principally till and glaciofluvial sediment. The latter two segments are underlain by WCSB bedrock, with the South segment associated with black shale of the Vermillion River Formation.

4.1 Mineralogy

The primary mineral constituents of soil parent materials are quartz, feldspar, amphibole, carbonate, and phyllosilicate and clay minerals, including illite-muscovite, smectite, chlorite, mixed-layer minerals, vermiculite and kaolinite (Fig. 3). Quartz and feldspar are abundant in all samples, with plagioclase concentrations consistently greater than those of

K-feldspar. Mixed-layer minerals tend to be more abundant in the northern half of the transect, and smectite preferentially occurs in glacial deposits of the South and North Dakota segments. Although widespread and abundant in till and glaciolacustrine deposits of the Interlake, South, and North Dakota segments, carbonate minerals were not identified in the northernmost glaciolacustrine deposits. In Interlake till, dolomite is more abundant than calcite. In the South and North Dakota segments, unlike overlying soil parent materials, black shale bedrock is dominated by quartz and contains no amphibole, chlorite, mixed-layer minerals, or vermiculite.

Although mineral suites comprising the <0.002-mm and the <0.063-mm fractions are similar, the <0.002-mm fraction is preferentially enriched in kaolinite, illite/muscovite, smectite and chlorite, and depleted in dolomite and amphibole. In South and North Dakota segments, the <0.063-mm fraction is enriched in plagioclase and K-feldspar compared to the <0.002-mm fraction, and the North Dakota samples have trace concentrations of opal in the <0.002-mm fraction.

4.2 Geochemistry

Till in the Interlake segment contains the lowest concentrations of total SiO_2 , Al_2O_3 , K_2O , and Na_2O , the greatest concentrations of total CaO and MgO (Fig. 4), and it is characterized by greater geochemical variability between sites than glaciolacustrine sediments. In the North segment, concentrations of lithophile elements indicative of silicate minerals (e.g., Al, Si, Na, K) decrease progressively southward toward the northern margin of the Paleozoic Platform; exceptions occur in the southernmost samples which overlie, and presumably contain, sandstone and shale (e.g., Red River or Winnipeg formations).

Profiles for the trace elements Cu, Zn, Ni and Cr show wide variations in geochemical concentration (level) and range (relief) (Fig. 5). Two of the 3 glaciolacustrine sediment samples overlying either Red River or Winnipeg formations are notably Cr- and Ni-rich. In the North Dakota and South segments, soil parent materials are Zn-rich. In the North and Interlake segments, two sample populations are distinguished by geochemical level, with net concentrations in the element-rich population decreasing southward.

4.3 Grain size

Element concentrations are typically greater in the <0.002-mm fraction than in the <0.063-mm fraction (Fig. 6). Calcium and Mg are exceptions having mean concentrations greater in the <0.063-mm fraction. Between grain-size fractions, geochemical properties have no significant linear correlations.

5. Discussion

5.1 Mineralogy and provenance

The soil parent materials (soil C horizon, 50 – 80 cm depth) are derived from 3 compositionally distinct bedrock terrains associated with igneous and metamorphic Shield bedrock, carbonate sediments of the Paleozoic Platform, and clastic sediments of the WCSB (Fig. 1). Soil parent materials represent till, glaciolacustrine and glaciofluvial deposits. The fine-grained character of glaciolacustrine sediments (clay-silt) is consistent with depositional environments unaffected by near-shore reworking.

The mineralogical profiles (Fig. 3) indicate that Shield-derived minerals are predominantly quartz, plagioclase, K-feldspar, amphibole and phyllosilicates, including chlorite, mixed-layer and vermiculite minerals; the latter two minerals may represent altered chlorite. Carbonate minerals, including dolomite and calcite, are derived from Paleozoic sedimentary bedrock; an apparent kaolinite association with Interlake till may indicate its occurrence in underlying bedrock. The WCSB bedrock is associated with quartz, plagioclase, K-feldspar, smectite, kaolinite, and with opal. It may also contain illite/muscovite.

From regional ice flow trends, all glacial transport directions were southward. Although transport patterns in glacial lakes are not known, the sediments are derived from the equivalent grain-size fraction of till in the lake catchment. In glaciolacustrine deposits of the North segment, concentrations of carbonate minerals derived from bedrock of the Paleozoic Platform decrease northward.

5.2 Mineralogy and Geochemistry

Mineral-element associations are inferred through empirical relations between geochemical properties and mineralogy and by the relative effects of aqua regia on different minerals (Räsänen et al., 1992; Snäll and Liljefors, 2000). Most susceptible to aqua regia digestion are carbonate and sulfide minerals, organic matter, Fe-Mn compounds, and Mg-bearing trioctahedral phyllosilicates. Amphibole and dioctahedral phyllosilicates, including illite/muscovite, are comparatively unaffected. For soil parent materials, it may be presumed that secondary Fe-Mn compounds and organic matter are either minimal or not present in the samples. On that basis, the minerals available for aqua regia digestion are sulfide, carbonate, and Mg-bearing phyllosilicates; as more common rock-forming minerals, the latter two minerals are more likely act as geochemical controls.

Statistically significant linear correlations between elements are commonly observed in large, multi-element regional geochemical datasets that may not indicate causal relations. Such correlations may arise either where elements occur in fixed proportions in a common mineral host, or where they occur in different mineral hosts having constant proportions in samples, or both. In either case, covariant changes in element concentrations reflect change in element-poor mineral concentrations.

Strong linear correlations for aqua regia-soluble Ca and Mg with inorganic C (CO_2) ($R^2 > 0.99$; $p < 0.0001$; $N = 37$) indicate these lithophile elements occur in carbonate minerals (Fig. 7a), and that in till of the Interlake segment their concentrations distinguish high- and low-carbonate till (e.g., Fig. 6) (Thorleifson and Matile, 1997). In carbonate-poor northern glacial lake sediments ($\text{CO}_2 < 0.1$ wt.%) (Kaszycki, 1989), Ca and Mg concentrations are < 2 wt.%, and in those samples likely occur in silicate minerals.

Strong negative linear correlation ($R^2 = -0.976$; $p < 0.0001$; $N = 37$) between the sum of total SiO_2 - Al_2O_3 - K_2O - Na_2O and CO_2 indicates that silicate mineral concentrations are inversely proportional to those of carbonate minerals (Fig. 7b). Silicate minerals, predominantly quartz, feldspar, amphibole and phyllosilicates, originate in Shield and WCSB bedrock, whereas carbonate minerals originate in bedrock of the Paleozoic Platform underlying the Interlake segment.

In glaciolacustrine samples of the North and Interlake segments, total Al_2O_3 and SiO_2 have positive linear correlation ($R^2 = 0.781$; $p < 0.0001$; $N = 23$) (Fig. 7c), with quartz and

feldspar likely dominant mineral controls. The greatest departures from the linear trend are for samples overlying, and presumably incorporating, bedrock of either the Red River or Winnipeg formations, or both, indicating those formations are compositionally distinct from Paleozoic bedrock elsewhere (J. Bamburak, 2006, pers. comm.). In the South and North Dakota segments, the increase in SiO_2 relative to Al_2O_3 is attributed to input of quartz-rich clastic sedimentary bedrock of the WCSB.

5.3 Comparison of total, near-total, and strong acid digestions

Elements occurring in aqua regia-insoluble forms and mineral residence sites are distinguished from those in aqua regia-soluble forms and residence sites by subtraction of partial analyses results from either total or near-total. Strong linear correlations and near-equivalence between near-total and aqua regia-soluble concentrations, indicate Cu, Ni, and Zn are predominantly soluble in aqua regia ($R^2 > 0.9$; $p < 0.0001$; $N = 37$) (Table 1 and Fig. 8).

In contrast, Cr and Ti are both aqua regia-soluble and aqua regia-insoluble, occurring in resistate minerals such as rutile, ilmenite, magnetite and chromite, as well as in phyllosilicate minerals. In deposits overlying Red River and Winnipeg formations in the North segment and WCSB bedrock in the South and North Dakota segments aqua regia-insoluble Cr and Ti are relatively most abundant. In deposits elsewhere, aqua regia-soluble and -insoluble Cr and Ti have strong linear correlations. Occurring in Shield-derived minerals, their proportions are unchanged by mixing with Cr- and Ti-poor carbonate bedrock detritus (Red River and Winnipeg formations excepted) in either till or glacial lake deposits.

5.4 Trace element – mineral host associations

Where elements may be apportioned among mineral hosts, the geochemical properties of overburden may be linked to bedrock provenance and physical geological process. Due to similarities in charge and ionic radius, Ba may substitute for K in common rock-forming minerals like K-feldspar and K-muscovite, and Sr for Na in Na-plagioclase and Na-amphibole (Krauskopf, 1967, p. 585). Strong linear correlations ($R^2 > 0.9$; $p < 0.0001$; $N = 37$) between aqua regia-insoluble Ba and K, and Sr and Na (Fig. 9) likely reflect the

geochemical properties of feldspars because they are the most abundant minerals. Slight differences in Ba-K proportions distinguish minerals derived solely from Shield terrain (e.g., Shield and Paleozoic bedrock; Fig. 9b) from those that also include a WCSB mineral component.

In North and Interlake samples, aqua regia-soluble trace metals (Cr, Ni, Zn, Cu) and K have strong linear correlations with aqua regia-soluble Al ($R^2 > 0.89$; $p < 0.0001$, $N=37$) (Fig. 10). The correlations indicate the trace elements occur in Al- and K-bearing minerals decomposed by aqua regia, and that their geochemical variation reflects variation in the proportions of the insoluble Shield-derived silicate minerals (e.g., quartz, feldspar, muscovite) and carbonate minerals that serve as geochemical diluents. As exceptions, glaciolacustrine deposits underlain by, and presumably incorporating, Red River and Winnipeg formations are relatively enriched in Cr and Ni, and depleted in K compared to Al, indicating geochemical-mineralogical differences specific to those formations.

The mineral hosts of trace metals are most likely K- and Al-bearing phyllosilicates, including chlorite, mixed-layer and vermiculite minerals, based on their occurrence in moderate concentrations determined through XRD analyses, their preferential dissolution by aqua regia, and their known associations with those trace metals as lattice impurities (e.g., Krauskopf, 1967). Among phyllosilicates, Mg-bearing trioctahedral minerals, including chlorite, are more readily digested by aqua regia than dioctahedral phyllosilicates like muscovite (Räisänen et al., 1992; Snäll and Liljefors, 2000).

In Interlake till, trace-metal bearing minerals are entirely Shield-derived. As a result, their concentrations are inversely proportional to the content of carbonate minerals, a relation clearly shown by strong negative correlations between aqua regia-soluble trace and lithophile elements and CO_2 (Fig. 11). For that reason, trace-metal background variation in the Interlake segment reflects both glacial history and glacial processes associated with the erosion, transport, and deposition of carbonate minerals.

5.5 Grain-size effects

Mineral partitioning among grain-size fractions results from surficial geological processes that either concentrate or dilute minerals on the basis of their density, size and

resistance to comminution, among other physical properties (Shilts, 1993, 1995). Due to partitioning, trace-element concentrations differ among grain-size fractions, with geochemical enrichments characteristic of the <0.002-mm fraction reflecting preferential enrichment of metal-bearing clay and phyllosilicate minerals in this fraction.

For Cd, the combined effects of mineral partitioning and provenance on geochemistry are illustrated by comparison of the <0.063-mm and <0.002-mm grain-size fractions (Fig. 12). In both fractions, aqua regia-soluble Cd concentrations greater than 0.5 mg/kg (the lower detection limit) are restricted to soil parent materials containing Cd-rich black shale of the WCSB, but the bedrock associations and geographic extent of Cd hazard potential are best defined by analysis of the <0.002-mm fraction. In black shale, Cd may be associated with clay minerals, organic C, sulfides, and non-crystalline secondary compounds, all of which, with the possible exception of sulfide minerals, may be expected to preferentially partition into the clay-sized fraction due to their low resistance to glacial abrasion and comminution compared to silicate minerals like quartz and feldspar.

6. Summary and conclusions

In soil parent materials sampled along the Manitoba-North Dakota transect, geochemical variation reflects 1) provenance and mineralogy, 2) the physical actions of surficial geological processes affecting the geographic distributions, concentrations, and partitioning of minerals, and 3) analytical protocol defined by the grain size chosen for chemical analysis and the strength of decomposition.

The minerals in analyzed C-horizon soils are derived from 3 compositionally distinct geological terranes, including igneous and metamorphic Shield bedrock, carbonate sedimentary bedrock of the Paleozoic Platform, and clastic sedimentary bedrock of the Western Canada Sedimentary Basin (WCSB). They are distributed in surficial deposits of glacial, glaciolacustrine and glaciofluvial origin. Till is derived by glacial erosion of bedrock along the path of ice flow. Glaciolacustrine sediments are derived from their equivalent grain-size fraction in till (e.g. <0.063 mm), and have been transported and mixed in the glacial lake environment. Although minerals may have varied, potentially complex, compositional relationships to underlying bedrock, geological process models

may be used to simplify their distributions and to interpret geochemical variability, a concept long-known and applied in mineral exploration by drift prospecting.

The interpretation of geochemical background variation may be simplified in terms of mineralogy and provenance. Correlations between total lithophile element concentrations and CO_2 (Fig. 7b), for example, indicate that silicate mineral concentrations are inversely proportional to those of carbonate minerals, with proportional differences between Al_2O_3 and SiO_2 (Fig. 7c) reflecting differences in the proportions of feldspar and quartz in Shield and WCSB terranes.

Linear correlations also indicate that Cu, Ni, Cr and Zn occur in Al- and K-bearing minerals subject to aqua regia decomposition. Their hosts are principally phyllosilicate minerals, including chlorite, that preferentially partition into the <0.002 -mm fraction. Although Cu, Ni and Zn are entirely aqua regia-soluble, Cr and Ti are both aqua regia-soluble and -insoluble, likely occurring in chromite, magnetite and illmenite as well as phyllosilicate minerals. Such minerals are widespread in both Shield and clastic sedimentary bedrock.

Differences in the proportions of Cu, Ni and Zn relative to Al reflect differences in the geochemical properties of host minerals in Shield and WCSB bedrock terranes. In contrast, the proportions of Cr and Al are independent of mineral provenance. Departures from linear correlations indicate Red River and Winnipeg formations may have distinct geochemical-mineral associations.

In the Interlake and North segments, Cu, Ni, Cr and Zn concentrations are inversely proportional to carbonate mineral content. Originating primarily in Shield bedrock sources, the metal-bearing minerals were glacially transported during phases of net southward ice flow and mixed in varying proportions with carbonate minerals during deposition of high- and low-carbonate tills. Where geochemical background variation is subject to predictions through glacial process models, departures from modeled values serve to identify potential changes in either mineral provenance or metal sources.

In the North segment, northward decreases in CaO and MgO correspond with increases in Al_2O_3 , SiO_2 , Na_2O , K_2O and silicate mineral concentrations. The inverse geochemical relationships reflect northward transport of carbonate minerals in a glacial lake system held against remnant glacier ice in Hudson Bay. Although glacier ice in the

Hudson Bay Lowlands would have overlain Paleozoic carbonate bedrock, the systematic northward decreases in carbonate mineral content indicate either that the primary source of carbonate minerals was Interlake till and bedrock, or that carbonate depletion may somehow be associated with regional variation in postglacial weathering and soil formation (e.g., Kaszycki, 1989).

Due to mineral partitioning, the selection of grain-size fraction for chemical analysis affects the portrayal of geochemical background and the interpretation of provenance. In contrast to the <0.063-mm fraction, Cd in the <0.002-mm fraction better illustrates the geographic extent of Cd-rich black shale in southern Manitoba and North Dakota because the Cd-bearing minerals and compounds derived from black shale preferentially concentrate in the clay-sized fractions of glacial deposits.

For environmental and human health protection, the geochemical properties of the <0.002-mm fraction appear most relevant to estimating exposure and hazard potential. Not only is that grain-size fraction preferentially enriched in trace elements (Cu, Ni, Zn, Cr, Cd), but the minerals comprising that fraction are also most likely moved along exposure pathways associated with ingestion and inhalation.

This study indicates how knowledge of geological provenance, process, and past simplifies the interpretation of geochemical background variation defined by regional geochemical surveys. In so doing, it also refines the interpretation of geochemical hazard potential in terms of analytical protocol, expressed in grain size and strength of analytical decomposition.

Acknowledgements

This paper represents a contribution to the North American Soil Geochemical Landscapes Project for the Environment and Human Health Program of the Geological Survey of Canada, Natural Resources Canada. Dr. R.G. Garrett and Dr. D.B. Smith are thanked for their constructive criticisms on the manuscript. Dr. W.W. Shilts and Dr. L.H. Thorleifson made suggestions that have led to further improvement; remaining faults are those of the author. GSC Contribution No.: 20060315.

References

Garrett, R.G., 2009. Relative spatial soil geochemical variability along two transects

- across the United States and Canada. *Appl. Geochem.*, this issue.
- Kaszycki, C.A., 1989. Surficial geology and till composition, northwestern Manitoba. Open File 2118. Geological Survey of Canada.
- Krauskopf, K.B., 1967. Introduction to Geochemistry. International Series in the Earth and Planetary Sciences. McGraw-Hill Inc.
- Lindsay, P.J., Shilts, W.W., 1995. A standard laboratory procedure for separating clay sized detritus from unconsolidated glacial sediments and their derivatives. In: Bobrowsky, P.T., Sibbick, S.J., Newell, J.M., Matysek, P.F. (Eds), *Drift Exploration in the Canadian Cordillera*. Paper 1995-2, B.C. Ministry of Energy, Mines and Petroleum Resources, 165-166.
- McGrath, S.P., Loveland, P.J., 1992. *The Soil Geochemical Atlas of England and Wales*. Blackie Academic & Professional, Glasgow.
- Moran, S.R., Arndt, M., Bluemle, J.P., Camara, M., Clayton, L., Fenton, M.M., Harris, K.L., Hobbs, H.C., Keatinge, R., Sackreiter, D.K., Salomon, N.L., Teller, J., 1976. Quaternary stratigraphy and history of North Dakota, southern Manitoba, and northwestern Minnesota. In: W.C. Mahaney (Ed.), *Quaternary Stratigraphy of North America*. Dowden, Hutchinson, and Ross Inc., Stroudsburg, PA, 133-158.
- Räisänen, M.L., Tenhola, M., Mäkinen, J., 1992. Relationship between mineralogy and the physico-chemical properties of till in central Finland. *Bull. Geol. Soc. Finland* 64, 35-58.
- Reimann, C., Äyräs, M., Chekushin, V.A., Bogatyrev, I., Boyd, R., Caritat, P. de, Dutter, R., Finne, T.E., Halleraker, J.H., Jæger, Ø., Kashulina, G., Niskavaara, H., Lehto, O., Pavlov, V., Räisänen, M. L., Strand, T., Volden, T., 1998. *Environmental Geochemical Atlas of the Central Barents Region*. NGU-GTK-CKE special publication. Geol. Surv. Norway, Trondheim, Norway.
- Reimann, C., Siewers, U., Tarvainen, T., Bityukova, L., Eriksson, J., Gilucis, A., Gregorauskiene, V., Lukashev, V.K., Matinian, N.N., Pasieczna A., 2003. *Agricultural soils in Northern Europe: a geochemical atlas*. *Geologisches Jahrbuch, Sonderhefte, Reihe D, Heft SD 5*, Schweizerbart'sche Verlagsbuchhandlung, Stuttgart.
- Salminen, R., Batista, M.J., Bidovec, M., Demetriades, A., De Vivo, B., De Vos, W., Duris, M., Gilucis, A., Gregorauskiene, V., Halavic, J., Heitzmann, P., Lima, A., Jordan, G., Klaver, G., Klein, P., Lis, J., Locutura, J., Marsina, K., Mazreku, A., O'Connor, P.J., Olsson, S.A., Ottesen, R.T., Petersell, V., Plant, J.A., Reeder, S., Salpeteur, I., Sandstrom, H., Siewers, U., Steenfelt, A., Tarvainen, T., 2005. *Geochemical Atlas of Europe. Part 1: Background information, methodology and*

- maps. Geological Survey of Finland, Espoo. Available from:
<<http://weppi.gtk.fi/publ/foregsatlas/index.php>>
- Shacklette, H.T., Boerngen, J.G., 1984. Element concentrations in soils and other surficial materials of the conterminous United States. U.S. Geol. Surv. Prof. Paper 1270.
- Shilts, W.W., 1978. Detailed sedimentological study of till sheets in a stratigraphic section, Samson River, Quebec. Bulletin 285. Geol. Surv. Canada, Bull. 285.
- Shilts, W.W., 1984. Till geochemistry in Finland and Canada. J. Geochem. Explor. 21, 95-117.
- Shilts, W.W., 1993. Geological Survey of Canada's contributions to understanding the composition of glacial sediments. In: Wheeler, J.O. (Ed.), Can. J. Earth Sci. 30, 333-353.
- Shilts, W.W., 1995. Geochemical partitioning in till. In: Bobrowsky, P.T., Sibbick, S.J., Newell, J.M., P.F. Matysek (Eds), Drift Exploration. Paper 1995-2, B.C. Ministry of Energy, Mines and Petroleum Resources, 149-166.
- Shilts, W.W., 1996. Drift exploration. In: Menzies, J. (Ed.), Glacial environments, sediment forms, and techniques. Butterworth-Heinemann Ltd., Oxford, Toronto, 411-439.
- Smith, D.B., Cannon, W.F., Woodruff, L.G., Garrett, R.G., Klassen, R., Kilburn, J.E., Horton, J.D., King, H.D., Goldhaber, M.B., Morrison, J.M., 2005. Major- and trace element concentrations in soils from two continental-scale transects of the United States and Canada. U.S. Geol. Surv. Open-File Rep. 2005-1253. Available from: <<http://pubs.usgs.gov/of/2005/1253/>>.
- Smith, D.B., Woodruff, L.G., O'Leary, R.M., Cannon, W.F., Garrett, R.G., Kilburn, J.E., Goldhaber, M.B., 2009. Pilot studies for the North American Soil Geochemical Landscapes Project – site selection, sampling protocols, analytical methods, and quality control protocols. Appl. Geochem., this issue.
- Snäll, S., Liljefors, T., 2000. Leachability of major elements from minerals in strong acids. J. Geochem. Explor. 71, 1-12.
- Teller, J.T., Fenton, M.M., 1980. Late Wisconsinan glacial stratigraphy and history of southeastern Manitoba. Can. J. Earth Sci. 17, 19-35.
- Thorleifson, L.H., Matile, G.L.D., 1997. Till geochemical and indicator mineral reconnaissance of northeastern Manitoba, Geological Survey of Canada. Geol. Surv. Canada Open File 3449 (diskette)
- Thorleifson, L.H., Garrett, R.G., Matile, G.L.D., 1994. Prairie kimberlite study – indicator mineral geochemistry. Geol. Surv. Canada Open File 2875 (diskette).

Table 1. Linear correlation coefficients (R) between trace elements determined after either total (INAA) or near-total (HF-HNO₃-HClO₃) and after partial (aqua regia: HNO₃-HCl) digestions.

Element	R ² Value	p
Al	0.867	<0.0001
As	0.272	0.1047
Ba	0.734	<0.0001
Ca	0.995	<0.0001
Co	0.96	<0.0001
Co	0.96	<0.0001
Cr	0.9	<0.0001
Cu	0.977	<0.0001
Fe	0.971	<0.0001
K	0.769	<0.0001
La	0.976	<0.0001
Mg	0.994	<0.0001
Mn	0.984	<0.0001
Na	-0.016	0.9267
Ni	0.975	<0.0001
P	0.989	<0.0001
Sr	0.256	0.1265
Ti	0.564	0.0002
Zn	0.975	<0.0001

Figure Captions

- Fig. 1** Location of sample sites along the transect overlain on generalized bedrock geology of Manitoba showing the Canadian Shield, and sedimentary bedrock of the Paleozoic Platform and the Western Canada Sedimentary Basin.
- Fig. 2** Generalized surficial geology of Manitoba showing the distribution of sample sites along transect.
- Fig. 3** Mineralogical profiles along the transect. Mineral concentrations are semi-quantitative (0 – not found. Increasing from 1 (trace) to 7 (abundant)).
- Fig. 4.** Geochemical profiles for major element oxides in <0.063 mm fraction determined after XRF (fusion) analysis. Vertical dashed lines connect two samples collected at the same site, and dashed circles indicate samples underlain by either Red River or Winnipeg formations.
- Fig. 5.** Geochemical profiles for Cu, Zn, Ni and Cr in the <0.063-mm fraction determined after aqua regia digestion. Vertical dashed lines connect two samples collected at the same site, and dashed circles indicate samples underlain by either Red River or Winnipeg formations.
- Fig. 6.** Box-and-whisker plots for geochemical analyses of the silt- and clay-sized (<0.063 mm) and the clay-sized (<0.002 mm) fractions.
- Fig. 7.** Bivariate plots showing linear correlations between: (a) aqua-regia-soluble Ca and Mg versus CO_2 ; (b) sum of major element oxides (Si, Al, K, Na) after total analyses and CO_2 ; (c) total Al_2O_3 and total SiO_2 . Dashed circles indicate samples underlain by either Red River or Winnipeg formations that are excluded from the correlation analysis.
- Fig. 8.** Bivariate plots showing linear correlations between aqua-regia-soluble and total element concentrations. Linear correlations for the sample subset of the Interlake and northern Manitoba segments are shown by dashed lines. Dashed circles indicate samples underlain by either Red River or Winnipeg formations excluded from the correlation analysis.
- Fig. 9.** Geochemical profiles along the transect for aqua regia-insoluble Ba and Sr, estimated by subtraction of concentrations determined by aqua regia analysis from those determined by either total or near-total digestions. Linear correlations between Ba and K_2O , and Sr and Na_2O indicate the element pairs may be principally associated with K-feldspar and plagioclase, respectively. For samples overlying WCSB bedrock, the slight change in aqua regia-insoluble Ba- K_2O proportions indicates that the geochemical properties of WCSB K-feldspar may differ from that of Shield terrain.

Fig. 10. Bivariate plots of aqua-regia-soluble Cu, Zn, Ni, Cr and K with Al. For Interlake and northern Manitoba samples, excepting those underlain by either Red River or Winnipeg formations (indicated by dashed circles), strong linear correlations indicate the elements occur in constant proportions within overburden in association with Al- and K-bearing hosts, possibly phyllosilicate minerals.

Fig. 11. Bivariate plots of Interlake till for aqua-regia-soluble trace elements (Cu, Zn, Ni, Cr) and lithophile (Al, K) elements and CO₂ indicate that their concentrations are inversely proportional to those of carbonate minerals.

Fig. 12. Geochemical profiles along the transect for Cd in the silt- and clay-sized and in the clay-sized fractions. Due to mineral partitioning, Cd in the <0.002-mm fraction best indicates the geographic extent of the Cd-rich black shale source.

ACCEPTED MANUSCRIPT

Fig.1

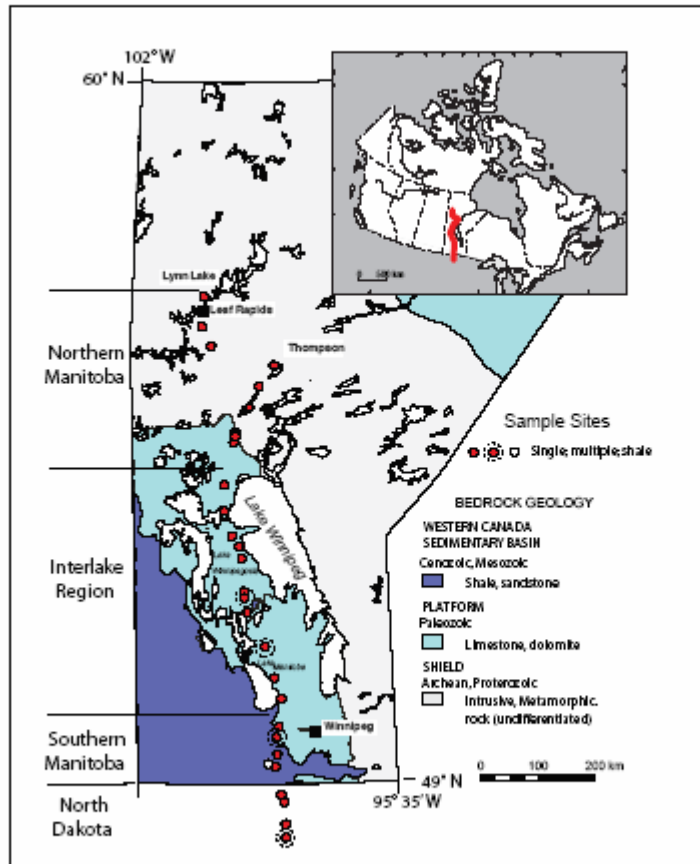


Fig.2

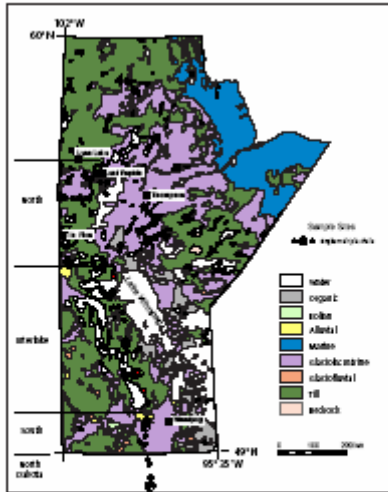


Fig.3

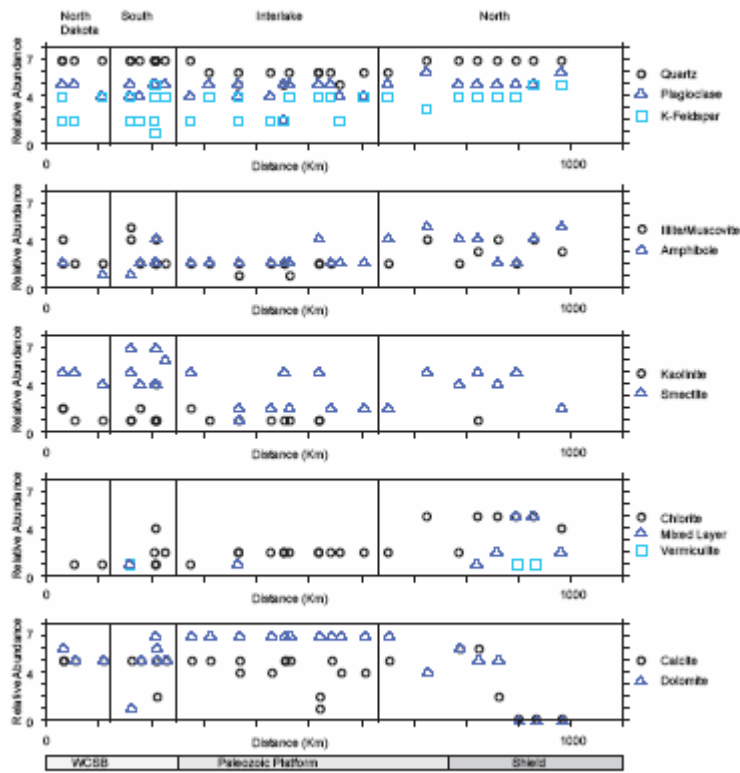


Fig.4

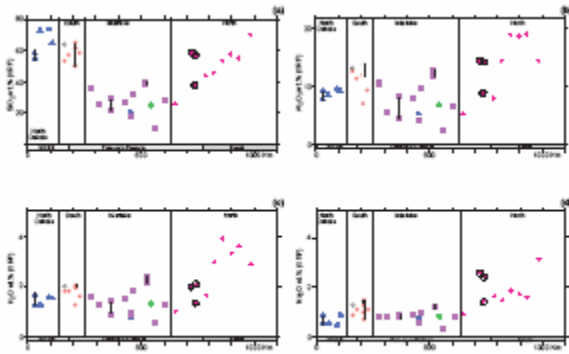


Fig.5

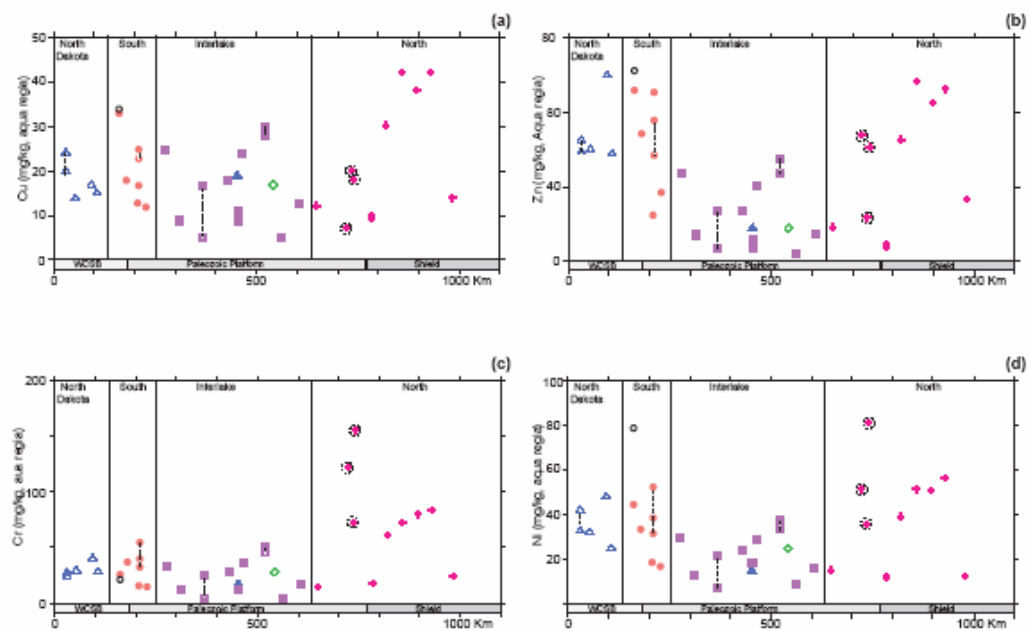


Fig.6

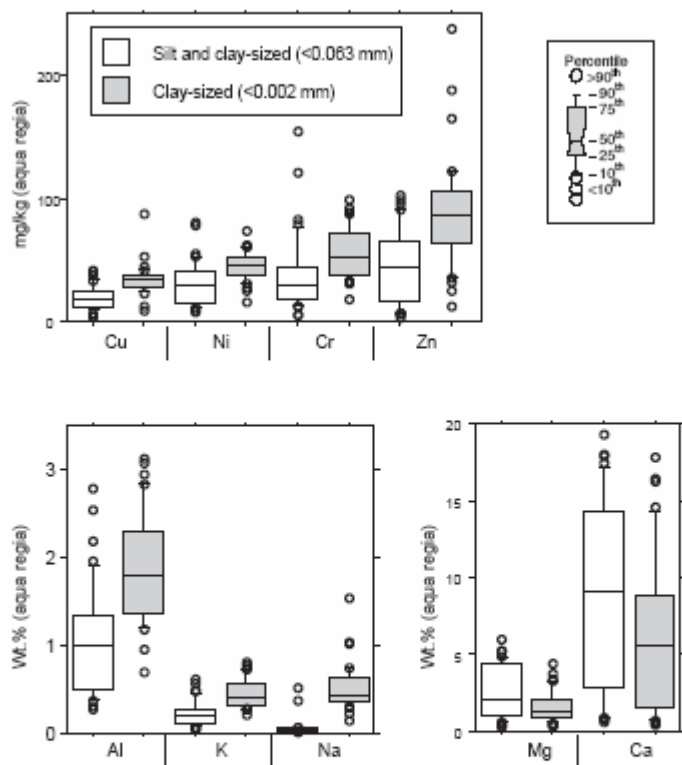


Fig.7

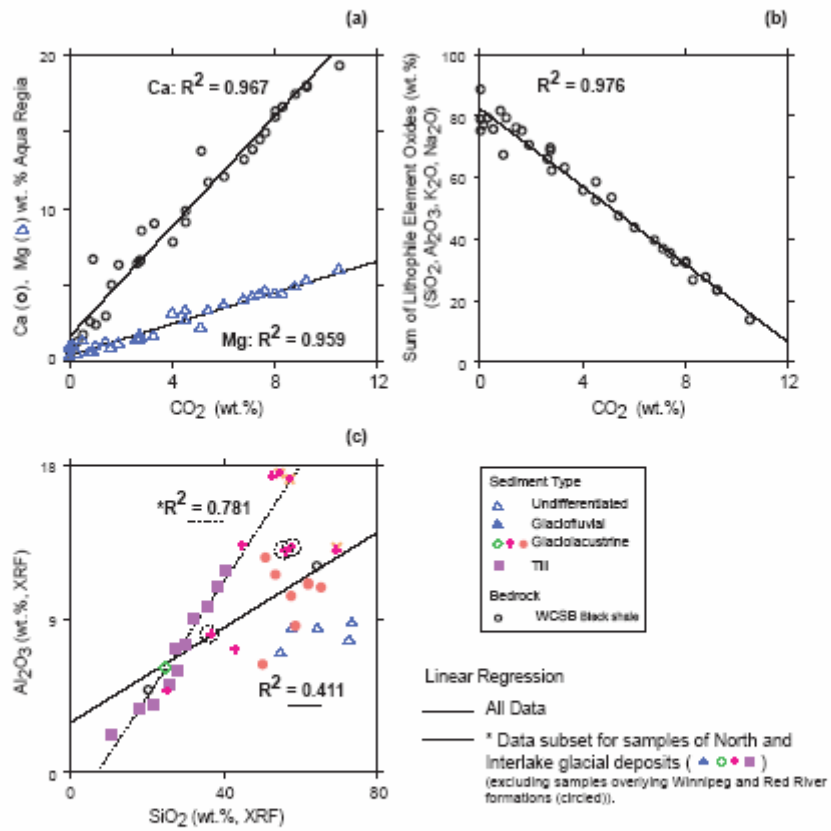


Fig.8

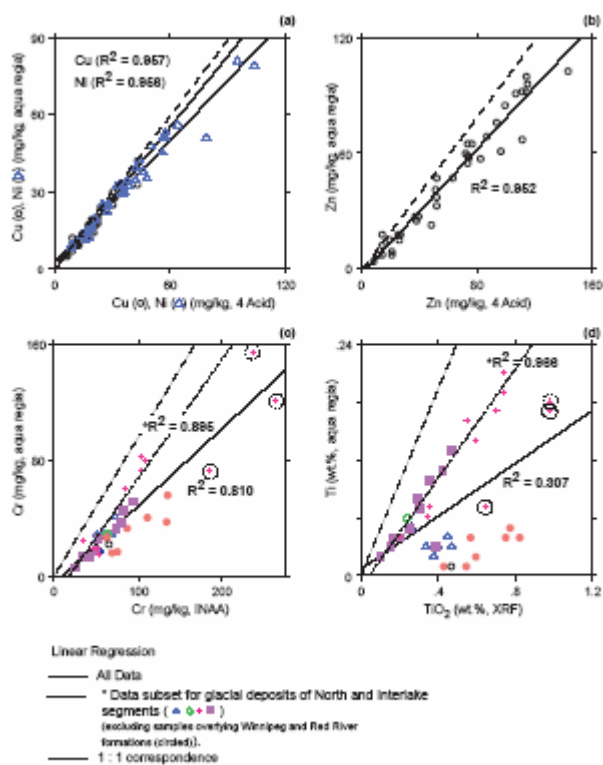


Fig.9

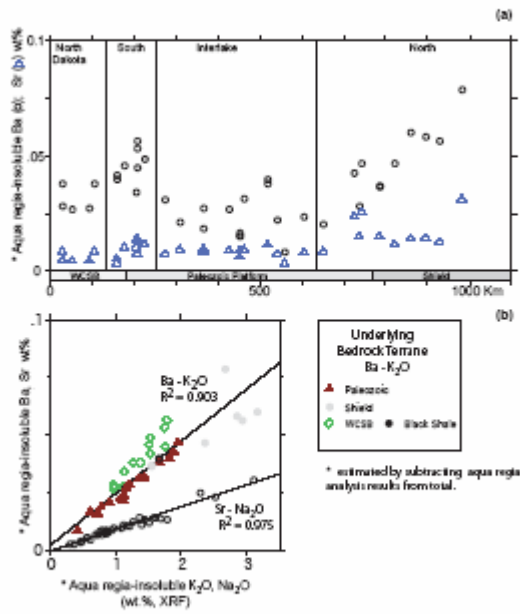


Fig.10

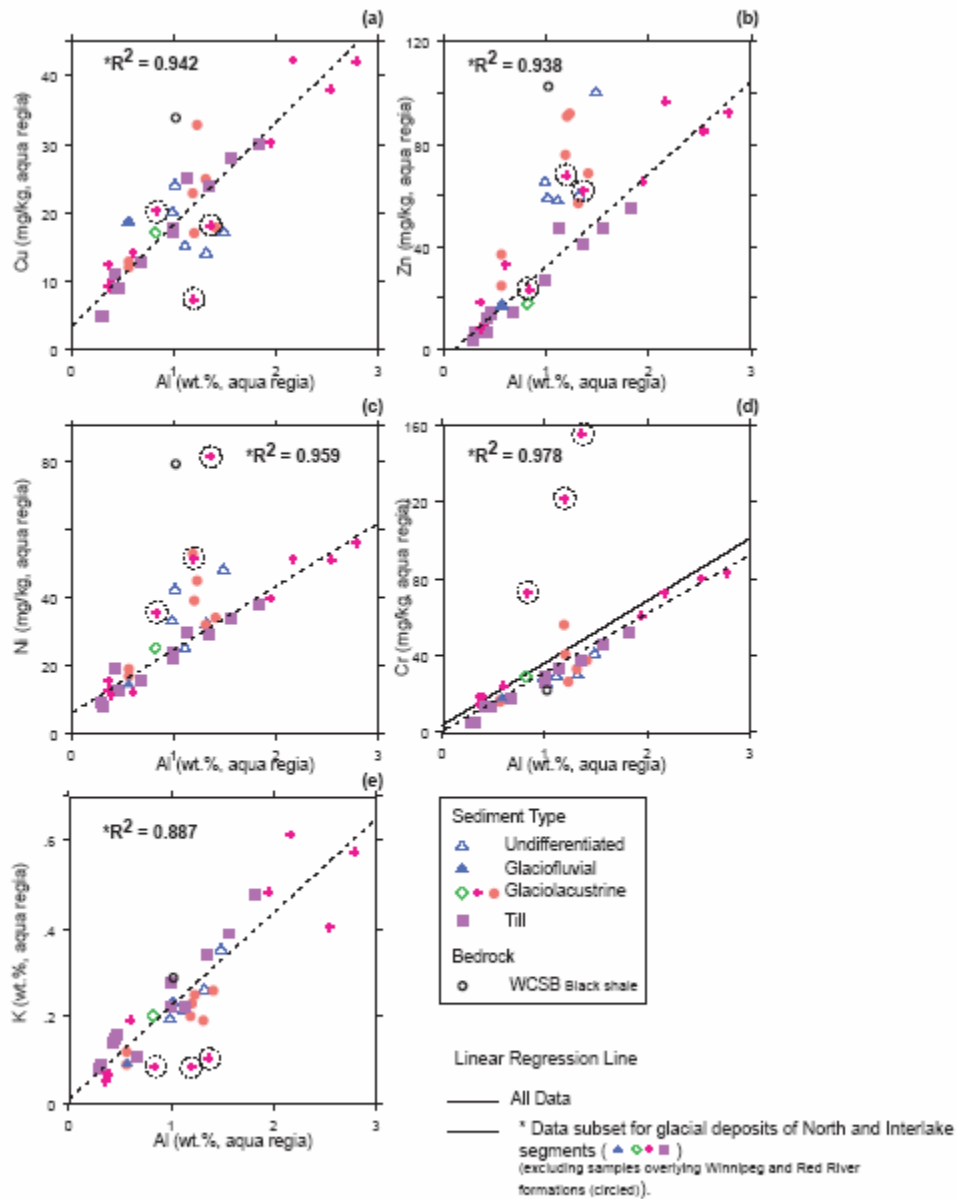


Fig.11

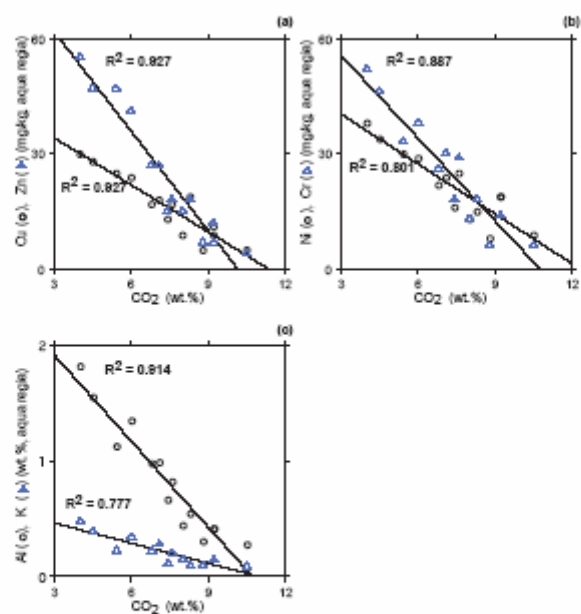


Fig.12

