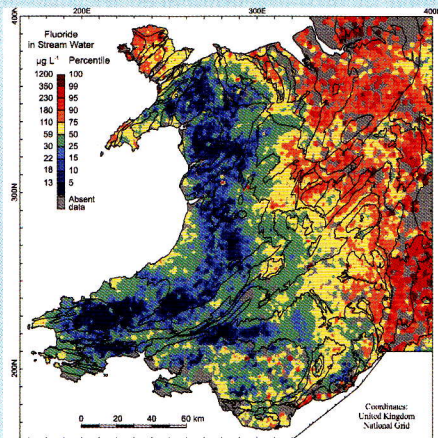


NATURAL DISTRIBUTION AND ABUNDANCE OF ELEMENTS

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I. NATURAL BACKGROUND

A widely recognized biological characteristic of a healthy and sustainable environment is diversity—as with biology, so with geology. Regions characterized by the presence of different bedrock units, and different surficial materials in areas affected by recent (geologically speaking) glaciation, develop varied landscapes that support differing ecosystems. Examples of varied landscapes range from Alpine and Cordilleran mountains, through gentler landscapes of rolling hills, to the glacial plains of Northern Europe and North America,

or similarly from the high Himalayas, through verdant foothills, across fertile plains to the desert of Sind. In the parts of the world characterized by stable geological platforms, where mountain building has not taken place for many hundreds of millions of years and there have been long periods of landscape development, peneplains are the eventual outcome. Their topography is gentle without mountains. High relief areas are largely limited to inselbergs or ravines and river valleys where, due to crustal uplift, modern rivers and streams are cutting down into and eroding the old land surfaces. These are the physical expressions of the underlying geology, but there is another changing characteristic that cannot be seen directly—the chemistry of the underlying rocks and sediments and the soils that lie upon them.

It is the soils that either directly, or indirectly, sustain the vast majority of life on terrestrial parts of Planet Earth. The plants people eat (cereals and vegetables) or use (e.g., wood for construction, fibers for fabric and line, maize or sugar cane for ethanol production) grow in the soil. Furthermore, soils interact with precipitation as it moves from surface to groundwater storage; they are vital to sustaining life.

Soils have developed over very different time spans, from those on the peneplains of Africa, Australia, and South America that are hundreds of millions of years old, to soils developed over the last few decades on recent vol-

canic material, and on freshly deposited silts from rivers that have overflowed their banks. Soils that have developed on glacial sediments are somewhat older. As the last ice retreated, about 8–12 thousand years ago, at the close of the Wisconsin (North America) and Weischelian or Würm (Northern Europe) Ice Ages, a bare landscape was exposed. What lay underfoot was poorly sorted glacial till, a mixture of eroded rock and sometimes previous soil, containing material from cobbles and large “rocks” down to finely ground mineral fragments. In places where glacial rivers had flowed under the ice, sinuous sand ridges called eskers were deposited. Where the rivers emerged from under the ice outwash fans were formed, and these became deltas when they flowed into glacial lakes. Sand dunes often formed near these glacial river outlets and back from lake shores as there was no vegetative cover to anchor the newly deposited sediments and save them from wind erosion as they dried. The soil cover had yet to form.

The soils that sustain life develop as an interaction between the solid rock or unconsolidated surface material, the climate, and biological and other physical processes. Over time vertical zonations called profiles develop as a function of the interaction of these processes (see also Plant et al., 2001, Figure 6). Many soils are characterized by an organic, carbon-rich black upper layer (the L, F, and A horizons); sometimes a sandy textured light-colored layer (the A_c horizon); commonly a brownish or reddish layer richer in iron and some other elements, organic matter, and minerals (the B horizon); and finally, the weathered soil parent material (the C horizon). Other characteristics develop where the soils are wet; in arid (desert) regions; or frozen in high northern and southern latitudes. In extreme northern and southern latitudes, polar deserts may form, or where there is sufficient moisture, permafrost may form. In the tropics the upper organic-rich A horizons are often thin due to the rapid degradation of the leaf litter and other organic materials present; below these iron-rich B horizons develop. In very old soils the B horizons may become cemented with iron oxides to form hard carapaces—variously named duricrust, ferricrete, or canga. One of the key outcomes of soil formation is that chemical elements commonly become vertically redistributed by the pedological (soil-forming) processes acting in the biogeochemical cycle. Within this major cycle many smaller cycles exist, such as that from soil to plant, back to soil, and soil to plant (see Section V for further discussion).

Natural backgrounds characterize the chemistry of rocks and surface materials, including soils, river and lake sediments, and biological tissues. Differences in

natural backgrounds arise due to landscape-forming processes, which in turn are influenced by diversity in the underlying geology. There is no one natural background level for any solid material in or on the Earth as the Earth is far too inhomogeneous (diverse). For there to be a single natural background for any substance it would have to be homogeneously distributed throughout the planet, and that situation is only approached in the atmosphere, where the major weather systems of the globe keep the atmosphere relatively well mixed in each hemisphere. Therefore, natural backgrounds are variable, and this chapter discusses and illustrates that reality.

Natural background concentrations of elements provide the pool of essential chemical elements required by biological processes; therefore, they are vitally important. Life on Planet Earth has developed in the presence of all the 97 naturally occurring elements of the periodic table. To varying extents biological processes employ these elements to fulfill specific biochemical tasks which ensure the continuation of life. However, in addition to essentiality there is toxicity (see also Chapter 8, this volume). A few elements, e.g., mercury, lead, and thallium, have no known essential role in sustaining life. On the contrary, at high levels in biota they may be toxic and cause dysfunction and eventually death. In this context, the case of mercury in fish is interesting. Although fish appear to be able to bioaccumulate mercury dominantly as highly toxic methyl-mercury species, without harm to themselves, the consumption of these fish by mammals leads to elevated mercury levels that can be cause for concern. Others, such as cadmium, are toxic at high levels in most animal life, but may be essential for metabolic processes that support life in some species (this is an area of current research). Other elements appear benign, for example, bismuth and gold; the latter is even used for dental reconstruction. Finally, a great number of elements are bioessential at some level. Calcium is necessary for building bones and shells; and iron is important in blood in higher mammals and vanadium and copper for similar roles in marine biota. Other major and trace elements, e.g., sodium, potassium, magnesium, copper, nickel, cobalt, manganese, zinc, molybdenum, sulfur, selenium, iodine, chlorine, fluorine, and phosphorus are also essential for a variety of biotic processes. For most elements it is a question of balance, enough to ensure the needs of essentiality and good health, but not too much which might cause toxicity. As Paracelsus stated 450 years ago and paraphrased to modern English: “The dose makes the poison.” It is the imbalance between amounts available naturally and

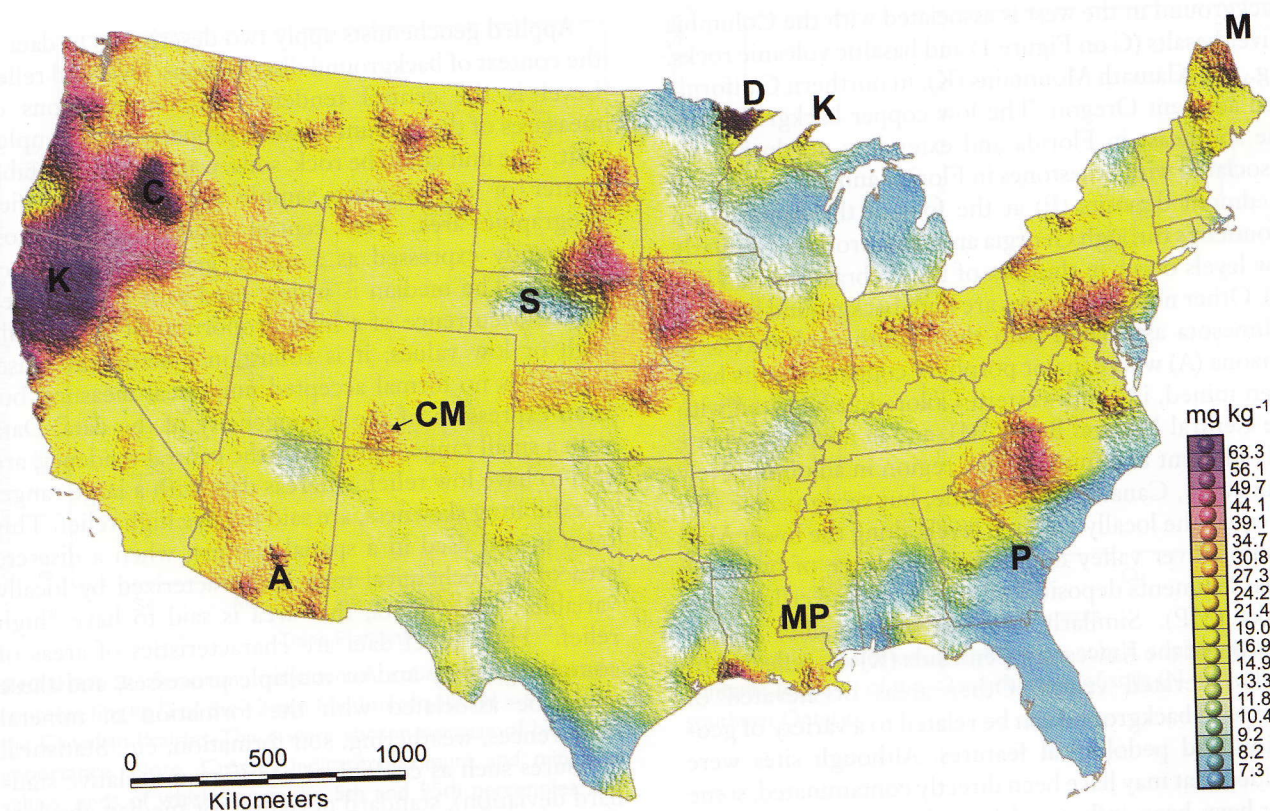


FIGURE 1 Copper content (mg kg^{-1}) of soils in the conterminous United States. (After Gustavsson et al., 2001 and Shacklette & Boerngen, 1984. Reproduced with the permission of the United States Geological Survey.)

those needed to sustain a healthy existence that poses the issues of medical geology.

II. A CHEMICALLY VARIABLE EARTH

An impressive way to demonstrate the chemical variability of the Earth's surface is with maps. Figure 1 displays the distribution of copper in the soils across the conterminous United States ($7.84 \text{ million km}^2$), which is about 5.3% of the Earth's land surface. What is important to know when using such a map and data is how the soil samples were collected, processed, and analyzed. These are critical facts that influence the conclusions drawn from geochemical data. In this instance the soils, characterized as natural supporting native vegetation or agricultural, were collected from 20 cm below the surface at sites generally over 100 m from roads. The soils were dried, disaggregated, and the fraction that passed a 2-mm stainless steel sieve was pulverized and directly analyzed by optical emission spectroscopy.

This method of analysis, which does not involve a chemical dissolution step, measures all of the copper present in the sample and is referred to as a "total" analysis. The samples used to prepare the map were collected by the U. S. Geological Survey between 1961 and 1975, and although over 25 years old, they still represent one of the few continental-scale depictions available (Shacklette & Boerngen, 1984; Gustavsson et al., 2001).

What are the noticeable features of these data? First, the map indicates they range from 7 to 63 mg kg^{-1} . This is almost an order of magnitude; however, in reality the individual 1323 sample analyses ranged from <1 to 700 mg kg^{-1} , almost three orders of magnitude, yet they were all collected from uncontaminated, background sites. The reduction in range in the scale from three to one order of magnitude is due to the smoothing process used to prepare the map (Gustavsson et al., 2001). Spatially, striking features are the high levels in the northwest versus the low levels in the southeast. An applied geochemist would state, the high background levels, etc. and Figure 1 is a graphic example of how natural background levels vary spatially. The high copper

background in the west is associated with the Columbia River basalts (C on Figure 1) and basaltic volcanic rocks, e.g., the Klamath Mountains (K), in northern California and adjacent Oregon. The low copper backgrounds in the southeast in Florida and extending northward are associated with limestones in Florida and old beach sand Piedmont deposits (P) at the foot of the Appalachian mountains through Georgia and the Carolinas. Similarly low levels occur in the area of the Nebraska Sand Hills (S). Other notable features are high background levels in Minnesota associated with the Duluth gabbro (D), in Arizona (A) where major porphyry copper deposits have been mined, in southwestern Colorado associated with the Central Mineral Belt (CM), and in northern Maine (M) adjacent to a mineral-rich region in adjoining New Brunswick, Canada. More subtle, but recognizable features are the locally elevated levels along the lower Mississippi River valley due to an abundance of overbank levee sediments deposited when the river overflowed its banks (MP). Similarly, the native (metallic) copper deposits of the Keweenaw Peninsula (K) are reflected by locally elevated values. Other areas of elevated or depressed background can be related to a variety of geological and pedological features. Although sites were avoided that may have been directly contaminated, some may have been influenced by airborne transport from local or major remote sources.

Clearly to speak of a single background level for copper in United States soils does the reality a great injustice. There is no one average background level. Backgrounds need to be regional and reflect contiguous areas where the processes influencing background levels are similar. Secondly and most importantly, background levels are not single average values but are ranges reflecting the natural heterogeneity of the entity being characterized.

However, having said this, average values are frequently published, e.g., Wedepohl (1995), Reimann and de Caritat (1998), and Kabata-Pendias (2000), for different sample media such as rocks, soil, and waters. These provide a useful service in establishing order of magnitude levels for the abundance of elements in various materials, and compilations such as Reimann and de Caritat provide a great amount of useful information. As a historical note, global averages are sometimes referred to as "Clarkes," after F. W. Clarke who was the chief chemist at the U. S. Geological Survey from 1884 to 1925. Clarke and Washington (1924) were the first persons to attempt to characterize geochemistry on a global scale with publication of an average composition for igneous rocks based on a collection of 5159 "superior" analyses.

Applied geochemists apply two descriptors to data in the context of background distributions: level and relief. Level is the central tendency of concentrations or measures of the amount of some property for a sampled unit. The unit could be rock, soils, waters, and vegetable matter or any discrete sample type for a specified geographic area. The central tendencies are most frequently expressed as a mean, geometric mean, or median. The median is widely used as it is unaffected by the occurrence of a high proportion of abnormally high or low values; it is robust in a statistical sense. Relief has no formal accepted numerical measure, but is an expression of the homogeneity of the data. Data with a small range, tight about the central tendency, are said to have low relief, whereas data with a large range, or exhibiting skewness, are said to have high relief. This term is also used in a spatial context, when a discrete area of a geochemical map is characterized by locally variable, "noisy" data, that area is said to have "high relief." High relief data are characteristics of areas of complex geology and/or multiple processes, and these could be associated with the formation of mineral occurrences, weathering, soil formation, etc. Statistical measures such as coefficient of variation (relative standard deviation), standard deviation, or median absolute deviation have been used to objectively quantify relief. The key issue is that background is not sufficiently characterized by a single number. Background is characterized by a range of values and some quantification is desirable, whether it be quoting percentiles of the data distribution or the computation of some statistic. The advantage of quoting percentiles is that they involve no assumptions as to the statistical distribution of the data. These data are very often mixtures of several distributions related to different bedrock units or materials derived from them and different processes, e.g., the presence of mineral occurrences or weathering and pedological factors. The greater the diversity of an area described, the more likely is it that there are multiple data populations present.

It is common for data from areas not characterized by the presence of anthropogenic contamination, mineral deposits, or a particularly diverse geology to span in excess of an order of magnitude. Figure 2 presents box-and-whisker plots for trace element concentrations in the <2 mm fraction of 973 surface (0–20 cm) soils collected from the Canadian Prairies in 1992. These soils developed on glacial sediments derived dominantly from the sedimentary rocks—i.e., limestones and dolomites (carbonates), shales and sandstones—of the Western Canadian Sedimentary Basin, and to a lesser extent from Canadian Shield rocks to the

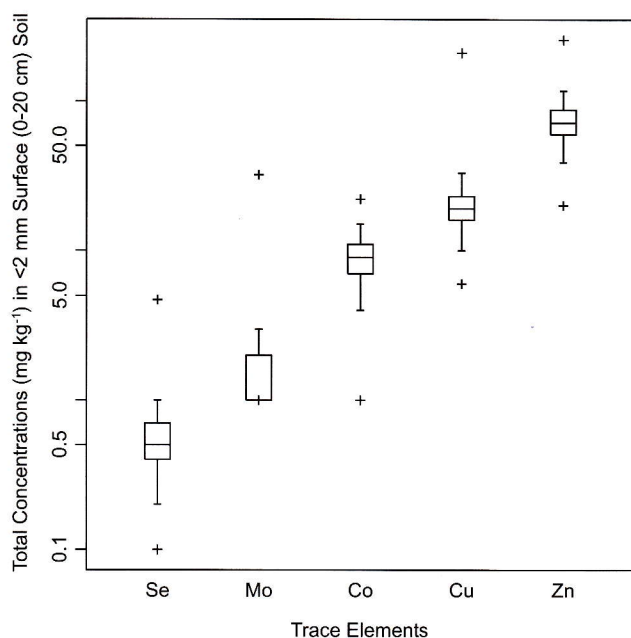


FIGURE 2 Selenium, molybdenum, cobalt, copper, and zinc contents (mg kg^{-1}) of the <2 mm fraction of soils ($N = 973$) from the Canadian Prairies. These were chosen because of biological importance. Note: Crosses indicate maximum and minimum values, ends of whiskers are the 5th and 95th percentiles, the box is bounded by the 1st and 3rd quartiles, and the bar indicates the median. If a notch is present rather than a bar, the notch indicates the 95% confidence bounds around the median, which is at the narrowest point.

northeast and north, and material from the Rocky Mountains to the west. As can be seen, the data span between one and one-and-a-half orders of magnitude. Most of the elements exhibit a positive skew, i.e., a greater abundance of higher values than lower. The cobalt data are an exception and exhibit a negative skew. The element with the greatest skew is molybdenum. Shales with abnormally high molybdenum levels occur in the region, and the distribution reflects this fact. The molybdenum data are characterized as having a greater relief than the other trace element data.

A soil survey undertaken using similar field sampling, sample preparation, and analytical protocols was undertaken in Ontario, Canada, in 1994. This survey included the Sudbury region which contains some of the largest nickel deposits in the world. For comparison, the same trace elements are plotted in Figure 3. The differences between the mid-50% of the data are small—molybdenum and cobalt levels in surface soil are higher in Ontario, while selenium levels are lower. What are different are the ranges and skewness of the data or their

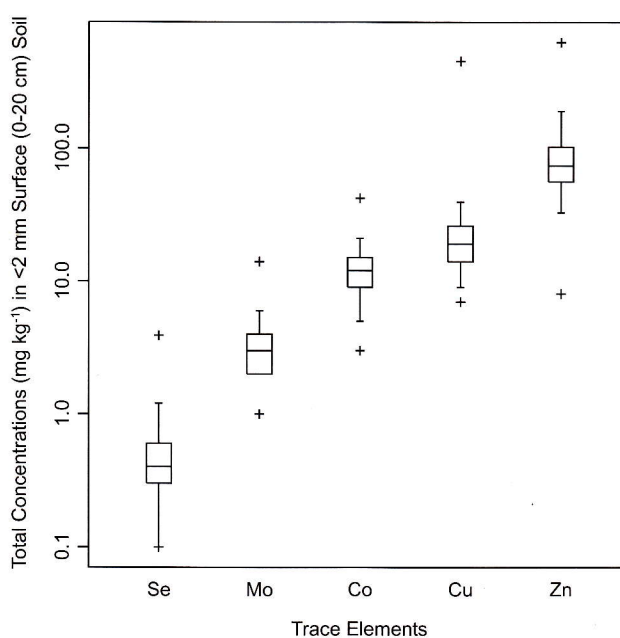


FIGURE 3 Selenium, molybdenum, cobalt, copper, and zinc contents (mg kg^{-1}) of the <2 mm fraction of soils ($N = 294$) from southern Ontario.

relief, which reflect the differences in geological diversity between the two survey areas. The range of the molybdenum data is greater in the Prairies, and the skew is greater reflecting the shales mentioned above. In the Ontario data, the ranges of the selenium, copper, and zinc data are larger which reflects the greater geological diversity (both older Shield rocks and younger Phanerozoic sediments) relative to the Canadian Prairies. Of particular significance is the increased positive skew or higher relief of the copper data, which reflects the presence of copper in the nickel deposits of the Sudbury basin.

The Sudbury ore deposits contain a wide range of metals present as sulfides and arsenides, and many are recovered commercially. Figure 4 presents the Ontario soil data for arsenic, cobalt, copper, and nickel. The deposits influence a small number of the survey sample sites, so the central parts of the distributions are not affected by their presence. Only the extremes for the major metals produced, i.e., nickel and copper are affected. The impact of the Sudbury basin, both as a geological and anthropogenic source (stack emissions), on what would be described as the background data distribution can be seen in Figure 5. The main part of the data spans one order of magnitude between 6 and 50 mg kg^{-1} nickel; two individuals (3 mg kg^{-1}) that fell

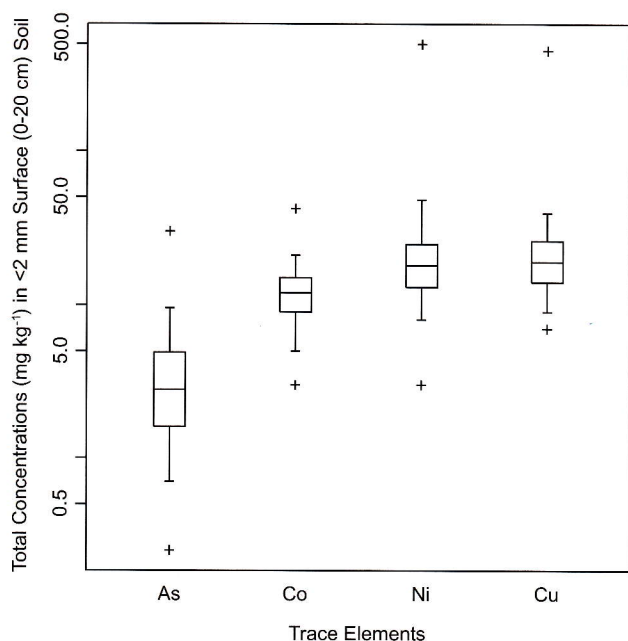


FIGURE 4 Arsenic, cobalt, nickel, and copper contents (mg kg^{-1}) of the $<2\text{ mm}$ fraction of soils ($N = 294$) from southern Ontario. These were chosen as they represent the Sudbury copper-nickel ore deposits.

below the detection limit of the analytical procedure (6 mg kg^{-1}) were arbitrarily set to half that limit; and most interestingly, a group of five individuals extend the range of the data a further order of magnitude to 500 mg kg^{-1} nickel. It is this latter group of samples that causes the data to have high relief and reflect the presence of the Sudbury basin, its mineral deposits, and its smelting facilities.

Background distributions may be influenced by naturally occurring high concentrations of trace elements and metals sometimes referred to as “natural contamination”, with the resultant data exhibiting a high relief. Such natural processes that lead to the accumulation of elements at specific sites in the Earth’s crust are what make them available to society for use. They raise concentrations to a level described as “ore”, i.e., that which can be extracted from the ground at a profit (noting that there are many different economic and social models to define profit). Often in such regions there are also areas of unusually low trace element and metal concentrations called alteration zones, which reflect where natural processes have removed metals to transport and concentrate them elsewhere. When this occurs the relief of data associated with ore elements can be very high. In general, “ore grades” exceed average crustal

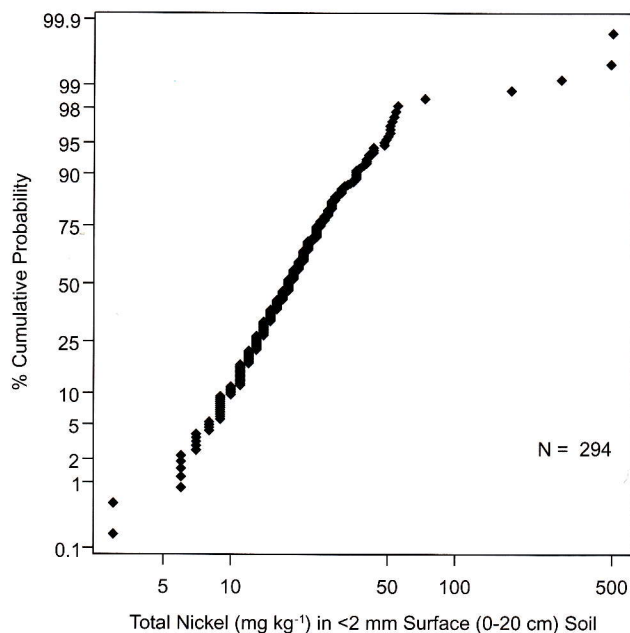


FIGURE 5 Cumulative probability plot of nickel contents (mg kg^{-1}) of the $<2\text{ mm}$ fraction of soils ($N = 294$) from southern Ontario, which demonstrate how mineral deposits are reflected by high outlying concentrations of an element in the ore.

abundance levels by two to four orders of magnitude (McKelvey, 1960), which results in natural ranges of trace element and metal concentrations in areas characterized by mineral deposits of four or more orders of magnitude. This depends on how much “ore-grade” material was incorporated in the samples collected. Two examples are provided below.

First, and to demonstrate that spatial scale has no effect on natural backgrounds per se, data for the nickel, copper, and zinc content of 292 glacial till samples collected from the walls of two adjacent trenches cutting across the Nama Creek copper-zinc deposit at Manitouwadge, Ontario, are presented in Figure 6. These trenches, about 300 m long and up to 4 m deep, were dug and sampled prior to the development of the deposit. The nickel distribution, as a measure of background—there are no nickel sulfides in the deposit—spans one-and-a-half orders of magnitude exhibiting low relief similar to the background distributions of most metals in the earlier examples. However, this is not the case for copper and zinc, which span over two-and-a-half orders of magnitude, exhibiting high relief, each due to the incorporation of ore-minerals containing these elements into the glacial till by the erosion of the mineral deposit. The additional order of magnitude

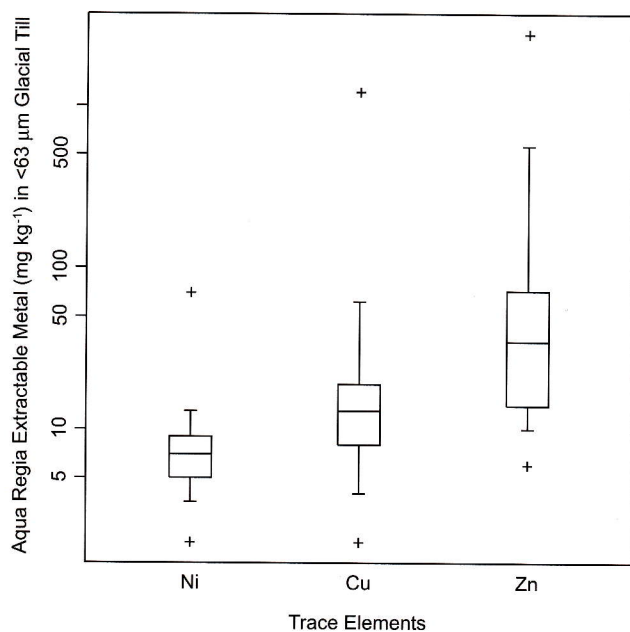


FIGURE 6 Nickel, copper, and zinc contents (mg kg^{-1}) of the $<63\ \mu\text{m}$ fraction of glacial tills ($N = 292$) from the Nama Creek deposit, Manitouwadge, Ontario. This demonstrates the impact of a copper-zinc deposit on the data with anomalously high copper and zinc levels in till samples derived from the erosion of the ore deposit.

reflects the presence of the mineral deposit, a factor which increases the geological and geochemical diversity in the area.

The second example is a regional stream sediment survey of approximately $80,000\ \text{km}^2$ from Goias State in central Brazil. The area is extremely diverse geologically with a wide range of sedimentary, igneous, and metamorphic rocks present, and it is blanketed by residual soils that have developed *in situ*. Of importance to the example is that the rocks range from "metal-poor" limestones and sandstones and their metamorphic derivatives to ultramafic igneous intrusives containing nickel and copper mineral occurrences. The distribution of nickel in the $<177\ \mu\text{m}$ fraction of the stream sediments is presented in Figure 7, where data span almost four orders of magnitude. These data are largely uninfluenced by anthropogenic activities, and therefore reflect natural processes. Four features are noteworthy: (1) 2% of these data were below the analytical detection limit of $2\ \text{mg kg}^{-1}$; (2) these and data up to $132\ \text{mg kg}^{-1}$ (99% of all the data) reflect the variation of a wide group of different rock types and soil-forming processes active in the region; (3) the upper tail of the distribution reflects samples collected from areas underlain by nickel-rich ultramafic rocks; and (4) the highest

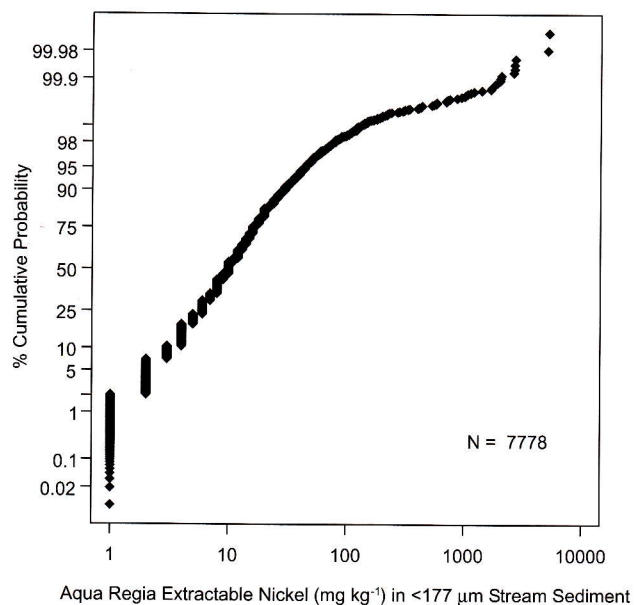


FIGURE 7 Cumulative probability plot of nickel (mg kg^{-1}) in the $<177\ \mu\text{m}$ fraction of stream sediments ($N = 7778$) from Goias State, Brazil. The flexure above $100\ \text{mg kg}^{-1}$ reflects the presence of nickel-rich ultramafic rocks, and the outlying values above $1500\ \text{mg kg}^{-1}$ reflect the nickeliferous pyrrhotite mineral occurrences within them.

levels, in excess of $1000\ \text{mg kg}^{-1}$, reflect the presence of nickel sulfide occurrences.

Thus the controlling factor in determining the range of natural background is not the size of an area, but the diversity of the geology present. High diversity, due to some combination of contrasting rock types and/or the presence of mineral deposits, leads to geochemical data that are similarly diverse, i.e., they are characterized by high relief. Another example of the presence of interesting patterns at widely different scales can be seen in Plate 3-1 of Darnley et al. (1995). This plate displays the copper stream sediment geochemistry of the island of St. Lucia, approximately $40\ \text{km}^2$, juxtaposed to the internal nickel chemistry of a grain of a platinum-bearing mineral $10\ \mu\text{m}^2$ in area. The difference in scale (area) is of the order of 10^{12} , yet well-designed sampling and analytical procedures at both scales reveal patterns of interest and geochemical significance.

Due to the diversity of geology and secondary environmental conditions, a vast number of regional and local backgrounds exist. This can be problematic when natural background distributions are used to establish national reference levels for regulatory purposes. For these to be effective they need to be very clearly defined as to what "environment" they represent, and they need to be based on adequately large sample sets. It is most

important that data are not used out of the context of their collection. This issue can be exacerbated if measures of central tendency are used as national reference levels, because this immediately implies that approximately 50% of all measurements relevant to the reference level will fall above the quoted value.

To avoid this problem, reference levels associated with environmental regulations are sometimes quoted at some other level, e.g., mean plus two standard deviations—notionally the 97.5th percentile of data derived from the estimated mean and standard deviation. In using this procedure an assumption has to be made, often implicitly with no discussion of the ramifications, as to the distribution of the data—normal, lognormal, or some other model. This can be fraught with problems, especially as the “geographic units” from which reference levels are derived get larger and more geologically and environmentally diverse. In such cases these data are likely drawn from a number of different distributions and agglomerated into a “mixture”. Often these mixtures appear to have lognormal distributions, despite the fact that many of the underlying components are more likely to have normal distributions (Vistelius, 1960). An alternative is to use a percentile of the natural background distribution as a reference value. An example of such a procedure is the use of an Ontario Typical Range 98 (OTR⁹⁸) value by the Department of Environment of the government of the Province of Ontario, Canada, which corresponds to the 98th percentile of the background data for a specific entity, e.g., residential lands. Every distribution has a 98th percentile; natural processes may be the cause of higher observed levels, and anthropogenic contamination may result in levels lower than the 98th percentile. Acceptable numbers of false positives or negatives, i.e., type I and II statistical errors, are chosen during the selection of any particular percentile. However, the OTR⁹⁸ level is used to trigger an investigation into whether the exceedance is due to natural phenomena or is the result of anthropogenic contamination. If it is the latter, appropriate actions are taken on a site-specific basis.

III. MINERAL CHEMISTRY— THE KEY TO THE DISTRIBUTION OF ELEMENTS IN ROCKS

A natural question is: Why is there such diversity in the chemistry of surface materials? The answer lies in the

composition of the individual minerals that compose rocks. Their properties are carried forward to other materials through erosional, weathering, and soil-forming processes, and are transferred to varying extents to waters that pass through these solid phase materials. In some respects the chemical diversity is self-fulfilling, as the main criteria that geologists use to “name” a rock, particularly in the field, are its mineralogy and texture (the shapes and interactions of and between the individual minerals). To have different names rocks must be visibly different from each other.

The major components of the common, abundant rock types are silicates. The exceptions are rocks such as limestones and dolomites and their metamorphic derivatives (marbles), which are composed of calcium and magnesium carbonates. Other exceptions include sedimentary rocks containing phosphates and iron carbonates. Oxide, hydroxide, sulfide, and other minerals can also host the trace elements found in biological systems.

Silicates and aluminosilicates are important minerals in geochemistry, particularly ferromagnesian minerals, feldspars, and phyllosilicates (e.g., micas and clays). These minerals all contain silicon and sometimes aluminum as major components. When they occur alone in a mineral they are present, respectively, as ubiquitous quartz and the rare corundum. Corundum occurs as the gemstones ruby and sapphire where the colors are induced by trace amounts of chromium (ruby), iron, or titanium (sapphire). The ferromagnesian minerals and feldspars are important as they, respectively, contain iron and magnesium, and calcium, sodium, and potassium as major components. The presence of these elements establishes a situation where other physically similar elements may enter the lattices of the mineral crystals. It is this phenomenon that results in the wide range of trace element concentrations observed in rocks.

Minerals are rarely “pure” and are commonly contaminated with a wide range of other elements present at “trace” concentrations. Pure minerals are so rare, and often beautiful, that they are only seen in museums and mineral collections. The key to understanding which trace elements enter different mineral crystal forms, by a process known as substitution, is through knowledge of the physical properties of ionic radius (Figure 8) and electronegativity (Figure 9).

One example is the ferromagnesian mineral olivine, which is a major component of many ultramafic and mafic rocks and forms the essentially monomineralic rock dunite. Its composition is $(\text{Mg}, \text{Fe})_2\text{SiO}_4$, which like many minerals is an intermediate form on a con-

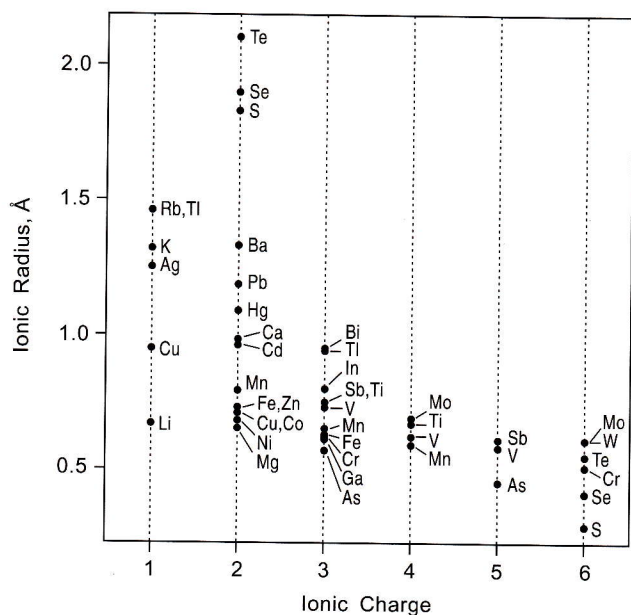


FIGURE 8 The relationship of ionic radius to ionic charge (valence) for major and trace elements of mineralogical and geochemical interest.

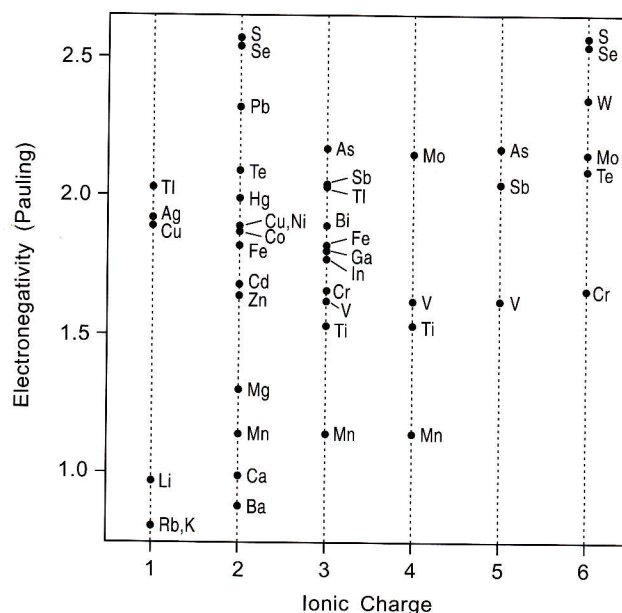


FIGURE 9 The relationship of electronegativity to ionic charge (valence) for major and trace elements of mineralogical and geochemical interest.

tinuous solid solution of two other minerals—pure Mg_2SiO_4 , forsterite, and pure Fe_2SiO_4 , fayalite—which themselves are rare. The ionic radii of iron and magnesium in their two-valent states are 0.74 and 0.66 Å, respectively. Thus in the solid solution form, olivine, there are crystal lattice sites that can just as easily be occupied by other two-valent ions, such as nickel (0.69 Å), copper (0.72 Å), cobalt (0.72 Å), zinc (0.74 Å), and with a bit more crystal stretch, manganese (0.8 Å). The inclusion of manganese is facilitated by the fact that there is a further solid solution between olivine and monticellite, $(Ca, Mg)_2SiO_4$, and the ionic radius of two-valent manganese lies between that for calcium (0.99 Å) and magnesium (0.66 Å).

When iron occurs in the three-valent form it can be incorporated into garnet group minerals, $Fe_3Al_2(SiO_4)_3$, which are common accessory minerals in many metamorphic rocks, and to a lesser extent, igneous rocks. Garnet chemistry can also be expressed as $3R^2O \cdot R^3O_3 \cdot 3SiO_2$, where the superscript number indicates the valence and the letter R indicates a metal. In this latter form it can be seen that three-valent aluminum (0.51 Å), iron (0.64 Å), chromium (0.63 Å), and titanium (0.76 Å) can enter the garnet crystal lattice. Garnets are truly remarkable in this fashion, and can host a wide range of divalent and trivalent metal ions. It is known that they occur widely at the base of the continental crust, as they come to the surface in rocks

named eclogites entrained in certain volcanic extrusives, and they are believed to be the host and “reservoir” for many of the trace elements stored deep within the crust.

Similar examples can be provided for the other important ferromagnesian minerals, and their capacity to host trace elements by substitution is most easily understood when their formulae are expressed in the same way as garnets. Thus, pyroxenes expressed as $R^2O \cdot R^3O_3 \cdot SiO_2$ and amphiboles expressed as $R^2O \cdot SiO_2$ can also contain aluminum and ferric iron and have very complex chemistries. They may also include hydroxyl groups and fluorine, epidotes expressed as $2R^2O \cdot R^3OH \cdot R^3O_3 \cdot 3SiO_2$, and micas, e.g., biotite, expressed as $K_2O \cdot 3(Mg, Fe)O \cdot 3(Al, Si)O_2 \cdot (OH)_2$. These examples again can have very complex chemistries. Because of the abundant sites for divalent and trivalent metal ions in sixfold coordination, and the ability for small cations such as aluminum to replace silicon in fourfold coordination, these ferromagnesian minerals are hosts for a wide range of trace elements.

The aluminosilicate feldspars also play an important role as hosts for larger ionic radius metal ions. Feldspar chemistry lies between three end members: anorthite ($CaO \cdot Al_2O_3 \cdot 2SiO_3$), albite ($Na_2O \cdot Al_2O_3 \cdot 6SiO_2$), and orthoclase ($K_2O \cdot Al_2O_3 \cdot 6SiO_2$). The physical structure of feldspars consists of SiO_4 and AlO_4 tetrahedra (silicon and aluminum in fourfold coordination) in a three-dimensional network. This network is elastic and

TABLE I. Classification of Elements as Lithophile, Chalcophile, Siderophile, or Atmophile

<i>Lithophile</i>	<i>Chalcophile</i>	<i>Siderophile</i>	<i>Atmophile</i>
C, O, P, H, F, Cl, Br, I, Si, Al, Fe, Mg, Ca, Na, K, Ti, Sc, Cr, V, Mn, Th, U, Nb, Ta, Sn, W, Be, Li, Rb, Cs, Ba, Sr, B, Y, Zr, Hf, rare earths (REEs), Ga, (Cd), (Zn), (Pb), (Cu), (Ni), (Co), (Mo), (Ti)	S, Se, Te, As, Sb, Bi, Ag, In, Ge, Tl, Hg, Cd, Zn, Pb, Cu, Ni, Co, Mo, Re, (Fe), (Sn), (Au)	Pt, Ir, Os, Ru, Rh, Pd, Au, (Fe)	N, O, C (as CO ₂), H, He, Rn, and other noble gases, (S as oxides), (Hg)

accommodates not only the large positively charged cations, calcium (0.99 Å), sodium (0.97 Å), and potassium (1.33 Å), but also strontium (1.12 Å), lead (1.2 Å), barium (1.34 Å), rubidium (1.47 Å), and thallium (1.47 Å), within its interstices.

Phyllosilicates are an important group of minerals in both rocks and their weathering products. They include silicate (e.g., talc) and aluminosilicate minerals commonly known as micas (e.g., phlogopite) and clays (e.g., montmorillonite), and may contain sodium, potassium, calcium, iron, and magnesium. These minerals have a sheeted mineral structure with pairs of sheets of SiO₄ tetrahedra held together tightly by cations; these pairs are held together loosely by other cations. In the case of the mica biotite, iron and magnesium provide the tight bonds and potassium the looser bonds. Muscovite mica is similar, but the tight bonds are provided by aluminum. A wide variety of cations may replace the iron, magnesium, and aluminum in the tight binding sites, and other elements may substitute for the potassium that loosely binds the sheets together. The breakdown of silicates and aluminosilicates due to alteration or weathering leads to the formation of a wide range of clay minerals, which host a wide range of cations in addition to silicon and/or aluminum. The mica and clay minerals with the greatest ability to support substitution with metal cations are generally those that employ iron and magnesium at interlayer sites, e.g., montmorillonite. In contrast, kaolinite or gibbsite only contains aluminum and silicon or aluminum, respectively.

The elements discussed above are commonly called lithophile (rock loving) and are distinct from other elements referred to as chalcophile, siderophile, or atmophile (Table I). The lithophile elements may occur as silicates, aluminosilicates, oxides, carbonates, sulfates, halides, phosphates, and vanadates, among other mineral forms in the natural environment.

An important second group are the chalcophile elements (Table I), which are characterized by forming sulfides, arsenides, antimonides, selenides, and tellurides. It is these compounds that form the ore minerals that are the source of the nonferrous metals used by society. Some of these minerals, particularly iron sulfides such as pyrite and marcasite (FeS₂), pyrrhotite (Fe_(1-x)S), and the sulfarsenide arsenopyrite (FeAsS), and to a lesser extent copper, zinc, lead, and molybdenum sulfides like chalcopyrite (CuFeS₂), sphalerite (ZnFeS₂), galena (PbS), and molybdenite (MoS₂), occur in many igneous and metamorphic and some sedimentary rocks. Due to the large amounts of these trace elements that can be held in sulfide and related minerals, it is not necessary to have abundant sulfides, etc., present in order to raise the levels of the chalcophile trace elements in rocks to quite high levels. As with silicate and aluminosilicate minerals, the chalcophile trace elements are often present as substitutions in commonly found minerals rather than in their own unique minerals. Again this is the result of fundamental physical properties, in this case electronegativity (Figure 9). As examples, silver and mercury replace copper in many copper minerals, cadmium and indium replace zinc in sphalerite, selenium and tellurium replace sulfur, and arsenic and antimony occur interchangeably in others and with sulfur. In iron sulfides copper, cobalt, and nickel commonly substitute for iron. In igneous and metamorphic rocks sulfides exist as blebs and crystals along the boundaries between the majority silicate and aluminosilicate minerals. In addition to this, they may occur within the rock-forming minerals along fracture planes. This is the result of a process known as exsolution, which occurs as rocks cool down and the individual rock-forming crystals are less able to accommodate incompatible components. The offending substances are then rejected to form discrete minerals along

TABLE II. Common Geochemical Associations

<i>Group</i>	<i>Associations</i>
Generally associated elements	K-Rb Ca-Sr Al-Ga Si-Ge Zr-Hf Nb-Ta Rare earths (REEs), La, Y Pt-Ru-Rh-Pd-Os-Ir Au-Ag
Plutonic rocks	
Generally associated elements	Si-Al-Fe-Mg-Ca-Na-K-Ti-Mn-Cr-V Zr-Hf-REEs-Th-U-Sr-Ba-P B-Be-Li-Sn-Ga-Nb-Ta-W-Halides
Specific associations	
Felsic igneous rocks	Si-K-Na
Alkaline igneous rocks	Al-Na-Zr-Ti-Nb-Ta-F-P-Ba-Sr-REEs
Mafic igneous rocks	Fe-Mg-Ti-V
Ultramafic igneous rocks	Mg-Fe-Cr-Ni-Co
Some pegmatites	Li-Be-B-Rb-Cs-REEs-Nb-Ta-U-Th
Some contact metasomatic deposits	Mo-W-Sn
Potassium feldspars	K-Rb-Ba-Pb
Many other potassium-rich minerals	K-Na-Rb-Cs-Tl
Ferromagnesian minerals	Fe-Mg-Mn-Ni-Co-Cu-Zn
Sedimentary rocks	
Fe-oxide rich	Fe-As-Co-Ni-Se
Mn-oxide rich	Mn-As-Ba-Co-Mo-Ni-V-Zn
Phosphatic limestones	P-F-U-Cd-Ag-Pb-Mo
Black shales	Al-As-Sb-Se-Mo-Zn-Cd-Ag-U-Au-Ni-V

After Rose, Hawkes, and Webb, 1979.

internal lines of crystal weakness or completely to a discrete mineral grain boundary.

Siderophile and atmophile elements are less important in the following discussion. The siderophile elements form alloys with iron and these are important sources of platinum group metals, together with gold, to society. The atmophile elements are ubiquitous in relatively hemispherically homogeneous atmospheres. Mercury is the only metal that occurs as a gas at "normal temperatures and pressures," and this permits its transport over long distances independent of fluvial systems.

Although not strictly a crystalline mineral phenomenon, many elements are associated with organic matter in sedimentary rocks and metamorphic rocks derived from them. This is due to two general processes: (1) the ability of organic compounds to sequester and adsorb trace elements, e.g., copper and mercury; and (2) the actual formation of metallo-organic compounds to

fulfill particular biochemical functions such as copper and vanadium in the heme of marine invertebrates. In the geological context, organic matter is only preserved in rocks under anoxic conditions, which due to the prevalent redox conditions are also sulfur-reducing environments that lead to the presence of sulfides. This is particularly important in the formation of rocks described as "black shales" that can become enriched in many trace elements.

As a result of these relationships geochemists have observed consistent patterns in the distribution of many elements. Some of the more interesting of these elements are presented in Table II. Several of the associations are related to mineral deposits, which are major natural sources of elements to the Earth's surface environment, and the processing of the ores can be major anthropogenic sources of contamination if appropriate emissions controls are not installed at processing plants and smelters.

In the secondary, weathering, environment most of the ferromagnesian and aluminosilicate minerals are unstable and break down to more hydrated forms, e.g., phyllosilicates, oxides, and hydroxides and residual silica (quartz). During this process the trace elements held in the rocks are liberated: some are removed in solution as surface runoff or enter groundwater, and others are incorporated into new minerals or sequestered by organic matter. Two key mineral forms capable of retaining trace elements are the phyllosilicates, minerals such as smectites and chlorites, and the oxides and hydroxides of iron and manganese. The phyllosilicates sequester trace elements by two processes: by cation exchange to constant electrical-charge sites on the tabular surfaces of the minerals, and by adhering to the broken edges of the clay particles where variable charge sites occur. Smectites are particularly effective in this role as they have large cation exchange capacities. The oxyhydroxides of iron and manganese formed during weathering are also effective in sequestering cations. This ability is enhanced when the oxyhydroxides are linked to humic or fulvic acids, which raises the charge on the oxyhydroxide surfaces. This effect is even more pronounced with the formation of humic colloids.

In contrast to the trace elements that are associated with minerals that break down in the weathering zone, those associated with resistate minerals that do not weather to any significant extent are retained in that mineral form in the soil and subsequent erosion products. Examples of resistate minerals are chromium in the mineral chromite; tin in cassiterite; niobium and tantalum in columbite-tantalite; zirconium and hafnium in zircons; and cerium, lanthanum, yttrium, and thorium in monazite.

IV. DIVERSITY IN THE CHEMISTRY OF ROCKS

The combination of the chemistry of minerals and their abundances in different rock types, which are defined upon a mineralogical and textural basis, leads to a varied rock geochemistry. Table III provides examples of estimated average values for the trace elements in the Earth's crust and different rock types. These estimated averages give no indication of the actual range observed in these individual rock types; such an estimate has never been made on a global basis, but it is likely at least one or two orders of magnitude. The variability behind the Continental Crust estimates can be implied from

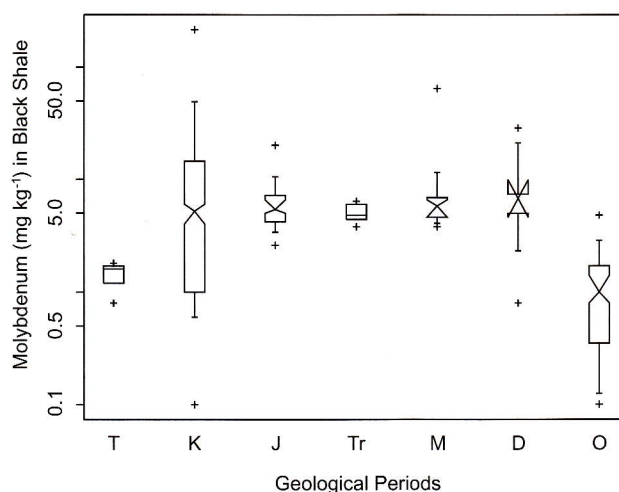


FIGURE 10 Distribution of molybdenum (mg kg^{-1}) by age in black shales, Manitoba, Canada. From youngest to oldest: T = Tertiary, K = Cretaceous, J = Jurassic, Tr = Triassic, M = Mississippian, D = Devonian, and O = Ordovician.

the variability for the estimates of individual rock types. These range from less than an order of magnitude for mercury to almost three orders of magnitude for nickel.

As an example of the variability associated with a single rock type, the example of black shales from Manitoba, Canada, is presented. These data come from 54 surface outcrop sites and drill holes in an area approximately 300 km wide (ENE–WSW) and 500 km long (NNW–SSE) along the eastern margin of the Western Sedimentary Basin. This area represents shales varying in age from Ordovician to Tertiary, spanning some 360 million years (Ma). Figure 10 displays the molybdenum data for the 476 samples subdivided by geologic period, oldest to the right and youngest to the left. The oldest (Ordovician, O) and youngest (Tertiary, T) black shales have lower molybdenum contents than the generally similar median valued Devonian (D) to Cretaceous (K) shales. However, what is outstanding is the variability of the Cretaceous (K) black shales, which extend over three orders of magnitude.

The Cretaceous shales span approximately 85 Ma of deposition in a sea that went through various transgressive (deepening) and regressive (shallowing) stages. The 333 black shales have been subdivided by stratigraphic formation (except for undivided Cretaceous rocks, K) in Figures 11–13. Figure 11 displays the by-age distribution of manganese (mg kg^{-1}), which forms a bowl shape with lowest manganese levels in the Favel (uKf) and Morden (uKm) Formations when the Western Interior Seaway was at its deepest. Manganese

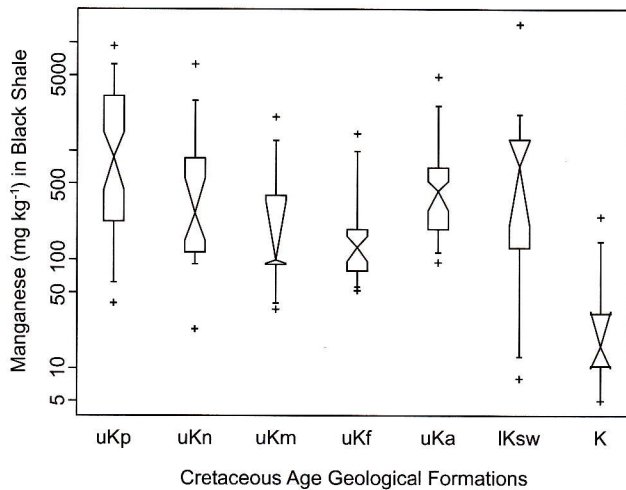


FIGURE 11 Distribution of manganese (mg kg^{-1}) in Cretaceous Age black shales, Manitoba, Canada, subdivided by Formation. Formations from youngest to oldest, where u as a prefix indicates upper Cretaceous and l indicates lower Cretaceous: uKp = Pierre, uKn = Niobrara, uKm = Morden, uKf = Favel, uKa = Ashville, IKsw = Swan River, K = undifferentiated, mostly lowermost Cretaceous, black shale.

levels increase in older Ashville (uKa) and Swan River (IKsw) and younger Niobrara (uKn) and Pierre (uKp) shales, which were deposited in shallower water. These variations reflect the fact that in the deep anoxic carbonate-poor waters of the Western Interior Seaway manganese was preferentially retained in the seawater. Figure 12 illustrates the distribution of molybdenum (mg kg^{-1}) in shales. Levels are highest in the deep water shales of the Favel Formation (uKf) where anoxic sulfide- and organic-rich sediments favored the sequestration of molybdenum, and the median molybdenum level is almost two orders of magnitude higher than for the youngest Pierre shales (uKp). Some of the Cretaceous shales, particularly the Favel (uKf), Morden (uKm), and Niobrara (uKn), are enriched in cadmium (Figure 13). At the surface, these shales were eroded from the Manitoba Escarpment and transported westward across the Canadian Prairies about 400 km during the Wisconsin glaciation at the close of the last Ice Age, and they have contributed to higher levels of cadmium in the agricultural soils of the region.

In some instances, large segments of the Earth's crust may exhibit consistent patterns of trace element enrichment. These features are known as geochemical provinces. Rose, Hawkes, and Webb (1979) provide the definition of these geochemical provinces as "a relatively large segment of the Earth's crust in which the

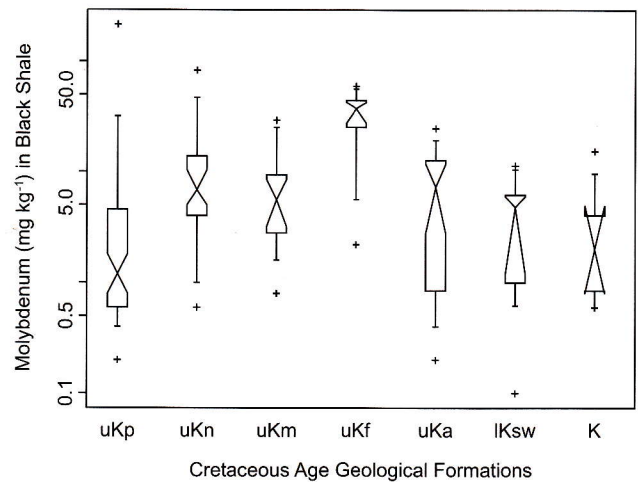


FIGURE 12 Distribution of molybdenum (mg kg^{-1}) in Cretaceous Age black shales, Manitoba, Canada, subdivided by formation. See Figure 11 for legend.

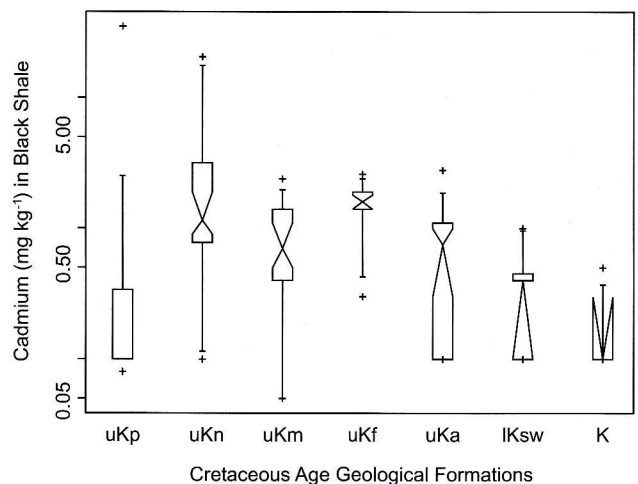


FIGURE 13 Distribution of cadmium (mg kg^{-1}) in Cretaceous age black shales, Manitoba, Canada, subdivided by formation. See Figure 11 for legend.

chemical composition is significantly different from the average." They go on to state: "One of the criteria of a bona fide geochemical province is that the characteristic chemical peculiarities should be recognizable in the rocks covering a substantial period of time." Examples of geochemical provinces are the Bear uranium province in the northwestern part of the Canadian Shield and the central European uranium province that includes parts of Germany, Poland, and the Czech Republic; the great tin province that spans from eastern

Australia, through Indonesia, western Malaysia, Thailand, and into China where rocks of many ages are enriched in tin; and the lesser known manganese province in northeastern North America including Maine and New Brunswick.

A second type of province, metallogenic, is of particular economic importance, and may have environmental and health consequences. Metallogenic provinces are regions of the Earth's crust that are characterized by the presence of mineral deposits and occurrences for particular metals, and they often are of a particular mineral deposit type. In any mineral district they are many more small mineral occurrences than economically exploitable mineral deposits. A distinction is made here between mineral occurrences and mineral deposits. Mineral deposits contain ore, i.e., that which can be extracted from the ground at a profit, using a sufficiently broad definition of profit to meet various societal needs. Metallogenic provinces may also be considered "mineral" provinces, as it is the presence of the metals in specific mineral forms at high concentrations that makes deposits exploitable. Examples are the copper deposits that occur in the western Americas extending from the southwestern United States through Central America to Peru, Bolivia, Chile, and Argentina; the prolific tin deposits coincident with the tin geochemical province of southeast Asia in Indonesia, western Malaysia, Thailand, and China; the Copper Belt deposits of Zambia and Zaire in central Africa; and the gold and base-metal deposits of the Abitibi Greenstone Belt in Quebec and Ontario, Canada.

The mineral forms for base- and precious-metals, apart from native (metallic) gold and platinum alloys, are sulfides, arsenides, antimonides, tellurides, and selenides that are far less stable in the surface weathering environment than the silicates, aluminosilicates, oxides, etc., which host the metals in common rocks. As a result, metals in mineral occurrences and deposits weather more easily and are transferred to soils, sediments, and waters. From a mineral exploration viewpoint their dispersion away from point sources facilitates exploration geochemical surveys. However, from a biological viewpoint this may be a good or bad outcome. If the metals are essential for life this may be beneficial; high metal levels may permit species that require such high levels, or are resistant to them, to flourish. If the metal species present is toxic, this will inhibit some life forms which may lead to an absence of biota or permit only certain hardy species to be present. It was well known that in the central African Copper Belt the high copper in the stream waters derived from the weathering of copper deposits was sufficient to be

toxic to the snails that were critical in the *Bilharzia* cycle. As a result, schistosomiasis was largely absent in the region. For those interested in the interaction of geology, geochemistry, and botany, readers are referred to Brooks (1972 and 1998).

The relationship between geochemical and metallogenic provinces is of some interest. By their nature geochemical provinces are low-entropy phenomena. In contrast, metallogenic provinces are high-entropy phenomena with extreme segregation of metals into spatially small discrete high concentration zones. Despite these contrasting characteristics, many metallogenic provinces lie within geochemical provinces, and it is assumed that the increases in regional background levels of the metals have provided part of the pool of metals that have been concentrated into the mineral deposits and occurrences. Reimann and Melezhik (2001) provided a discussion of the relationships between metallogenic and geochemical provinces in the context of a large (188,000 km²), low sampling density (1 site per 300 km²) regional geochemical study of surficial materials in Arctic Europe called the Kola Ecogeochemistry Project (Reimann et al., 1998). The authors noted that some significant metallogenic provinces were not recognized in the project they undertook, and also cast doubt on the value of the term "geochemical province." However, considering the very different nature of the two province types in terms of entropy, and the interaction of sampling density through search theory to the probability of recognition of the mineral occurrences of a metallogenic province with low-density field sampling programs (see Section V and Garrett, 1983), the death of these provinces as useful concepts is premature.

It is this underlying variability in rock chemistry, that is in turn due to the mineralogical and compositional variability of the rocks composing the Earth's crust, let alone the mineral deposits and occurrences that occur in them, that causes the geochemical variability in natural background levels in the surficial materials and weathering products discussed in the first section of this chapter.

Although tables of averages (Table III) are useful as general indicators of the element content of rocks, the variability behind them must never be forgotten. As noted and demonstrated above, that variability is considerable and can easily span up to three orders of magnitude for trace elements. Readers requiring average estimates for composition of both the Earth's crust, individual rock types, and other materials are referred to Wedepohl (1995), Reimann and de Caritat (1998), and Kabata-Pendias (2000).

TABLE III. Compilation of Average Geochemical Background Data for the Earth's Crust and Selected Rock Types

	Hg ($\mu\text{g kg}^{-1}$)	Pb (mg kg^{-1})	Cd (mg kg^{-1})	Cr (mg kg^{-1})	Ni (mg kg^{-1})	As (mg kg^{-1})	Cu (mg kg^{-1})	Zn (mg kg^{-1})	Ref.
Earth's crust	80	13	0.2	100	75	2	55	70	Taylor, 1964
	90	12	0.2	110	89	2	63	94	Lee & Yao, 1970
Upper continental crust	80	20	0.1	35	20	1.5	25	71	McLennan, 1992
		13	0.2	77	61	1.7	50	81	Lee & Yao, 1970
Igneous rocks									
Ultramafic	4	1	0.1	1600	2000	1	10	50	Turekian & Wedepohl, 1961
Mafic	13	6	0.2	170	130	2	87	105	Turekian & Wedepohl, 1961
Intermediate	21	15	0.1	22	15	2	30	60	Turekian & Wedepohl, 1961
Felsic (4)	39	10		55	30		60		McLennan, 1992
		19	0.1	4	5	1	10	39	Turekian & Wedepohl, 1961
Sedimentary rocks									
Sandstone	57	14	0.02	120	3	1	15	16	Faust & Aly, 1981
Limestone	46	16	0.05	7	13	2	4	16	Faust & Aly, 1981
Shale	270	80	0.2	423	29	9	45	130	Faust & Aly, 1981
Black shale		15	4.0	18	68	22	50	189	Dunn, 1990
		100		700	300		200	1500	Vine & Tourtelot, 1970

V. THE BIOGEOCHEMICAL CYCLE

The discussion in this chapter thus far has concerned the mineral kingdom. However, mineral-related processes only form one part of what is known as the biogeochemical cycle—the sum of the biotic and abiotic processes that move elements from rocks, to soils, sediments, and waters where they are incorporated into plants and animals and become parts of food chains. As these processes proceed elements are returned to soils, sediments, and waters and, given sufficient geological time, are incorporated into deposits that will be transformed to newly formed rocks. However, of more immediate interest is the small scale cycling that occurs at local levels.

Plants play a key role in the biogeochemical cycle; they are critical to soil formation in all but desertic regions. The acids that their roots produce to liberate nutrients from the minerals in the soil contribute to the breakdown of those minerals. Another source of organic acids that contributes to mineral decomposition is the decay of litter—fall as plant material decomposes in the surface layers of soil. As these acids percolate downward they solubilize and carry many elements with them to lower levels in the soil. This process is vividly demonstrated in the podzolic soils (Spodosols) of humid temperate zones. Organic matter accumulates in the topmost layers of the soils (the L, F, H, and A_h horizons), giving them their characteristic dark brown-black color. Immediately below this there is a “sandy,” colorless, leached (eluviated, A_c horizon) zone composed of mineral grains that have resisted corrosion and decomposition. Below the eluviated zone the soils are enriched in iron-oxyhydroxides, clay-sized materials, and to a lesser extent organic substances. Known as the B horizon, it is well developed in podzols and exhibits a rich red-brown coloration. Together, the humic-rich (A_h) top layer of the soil and the B horizon are sites of trace element, especially metal, accumulation due to the abundance of organic matter, smectites, clay minerals, and iron- and manganese-oxyhydroxides. The retention of trace elements in these horizons introduces a barrier in the biogeochemical cycle that halts circulation through the cycle for varying periods of time. Goldschmidt (1937) introduced the term “geochemical barrier” specifically for the retention of trace elements in humic-rich surface soil as it was a barrier to “flow” in the biogeochemical cycle.

As a result of the biogeochemical cycle, trace elements are dispersed into different materials, three

examples are provided below, i.e., one for stream waters (Wales), one for organic stream plant material (Sweden), and one for terrestrial plant material and a foodstuff called hard red spring wheat (Canada). A fourth example of mineral rich stream sediment is provided in Section V.

In recent years the British Geological Survey has applied new ultrasensitive water analysis procedures in the preparation of hydrogeochemical maps. Figure 14, drawn from Simpson et al. (1996), is an example of the distribution of fluoride in stream waters from Wales and adjacent parts of England as revealed by a suite of 17,416 analyses. There is a clear boundary between high F⁻ waters draining dominantly Permo-Triassic rocks in the east and low F⁻ waters draining older Paleozoic rocks to the west. These two rock types were laid down in very different environments: the older rocks in a variety of marine environments, and the Permo-Triassic rocks in a terrestrial environment that was desertic to the east along the western margins of the Zechstein Sea and later along the northwestern margin of the Tethyan Ocean. What is important here is that the different environments that either favored the retention of F⁻ in terrestrial environments or its retention in seawater have survived in excess of 200 Ma to influence ground and surface water chemistry today and have epidemiological consequences (Simpson et al., 1996).

The Swedish Geological Survey is unique among geological surveys in employing organic stream material for its national-scale geochemical survey program (Fredén, 1994). The reason for this choice of sample material, as distinct from the mineral-rich stream sediments commonly collected in other countries (see for example Figure 17), is that it provides data that better estimate the bioavailable amounts of trace elements present in the environment. Aquatic plants such as aquatic mosses and sedge (*Carex* L.) roots are in equilibrium with the stream sediments and waters in which they grow, and their composition reflects the available amount of trace elements. Although stream water compositions may vary seasonally, the composition of the mosses and sedge roots varies more slowly, smoothing out temporal variations in the water chemistry. This makes the survey data particularly effective for monitoring anthropogenic impacts that result in the dispersion of trace elements into the surficial environment, and detecting natural geological sources that may have an impact on the ecosystem. Figure 15 presents the stream plant chemistry for chromium in part of southern Sweden. The elevated levels in the western part of the map around Vänern and Trollhättan are associated with pollution from a smelter. Yet in the central

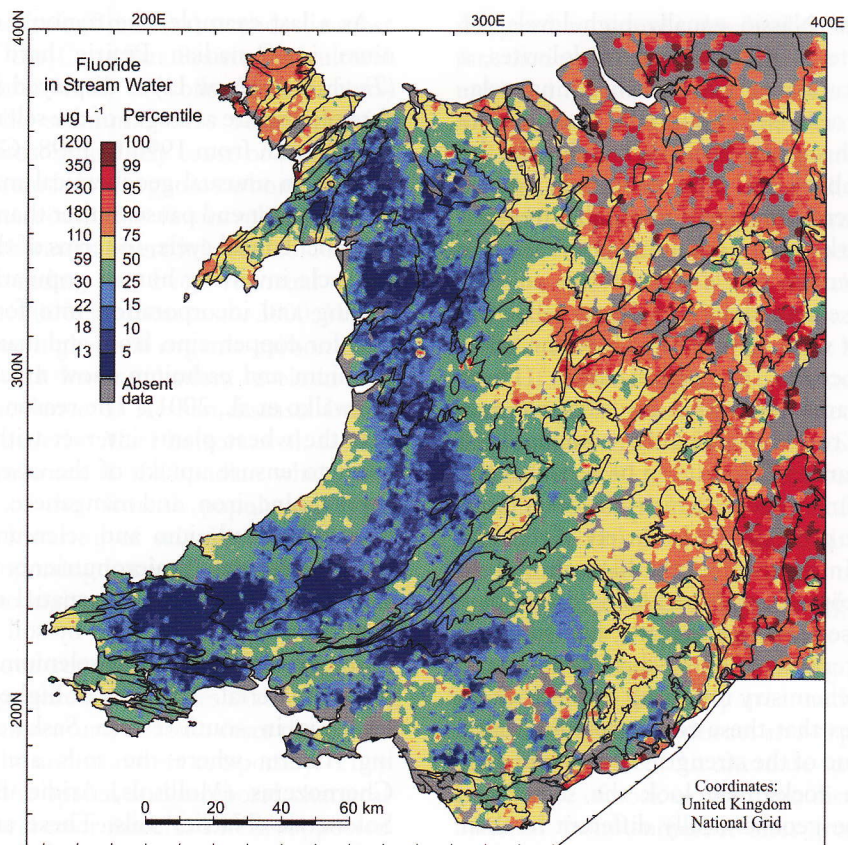


FIGURE 14 Fluoride ($\mu\text{g L}^{-1}$) in stream waters (N = 17,416) from Wales and adjacent parts of England. (Reproduced with the permission of the British Geological Survey and Pergamon Press.)

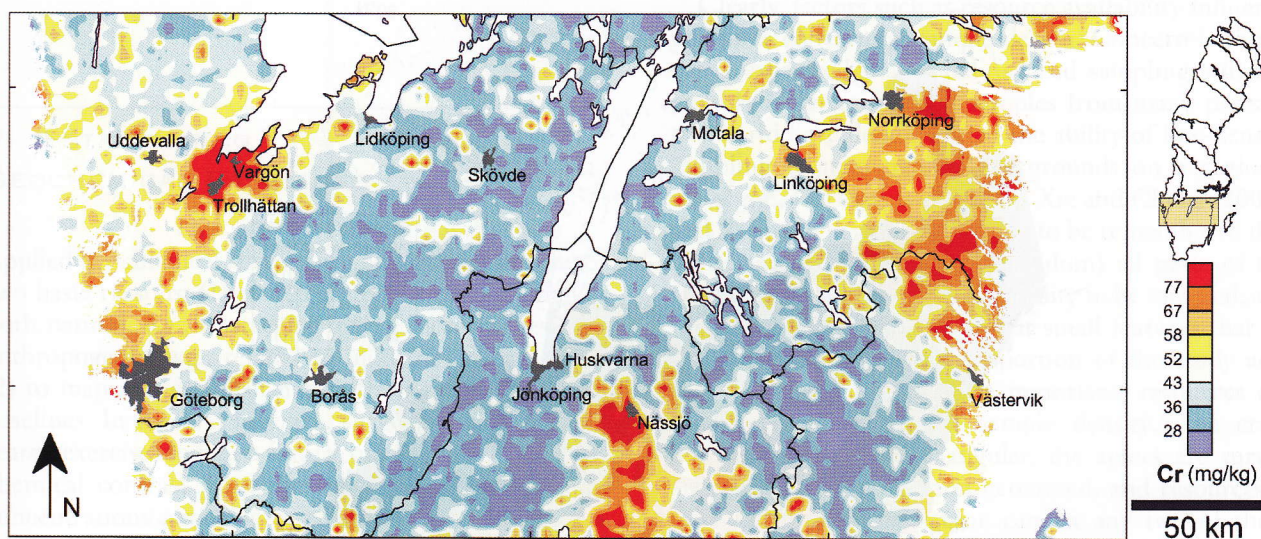


FIGURE 15 Distribution of chromium (mg kg^{-1} in ash material) in organic stream sediments in southern Sweden. (Reproduced with the permission of the Geological Survey of Sweden.)

part of the area near Nässjö equally high levels are observed which relate to the presence of dolerites, a mafic rock that is naturally enriched in chromium relative to most other rocks (see Table III). To the east-southeast elevated chromium levels occur due to the presence of small gabbro and ultramafic rock bodies. Another notable pattern occurs in a triangular area east of a line joining Norrköping, Linköping, and Västervik where elevated chromium levels characterize an area underlain by old basement granitoid, likely reflecting even older rocks that were incorporated into the granitoids by the processes of granitization. These chromium elevated areas lie within an extensive area of low chromium rocks dominantly composed of orthogneisses and granites. Thus it can be seen that the organic stream sediment geochemistry reflects both recent anthropogenic processes and a variety of regional geological features. In this context the high chromium patterns east of Linköping and Norrköping are of particular interest. These rocks are granitic, like so much of the area characterized by low chromium levels; however, a relict geochemistry reflecting earlier rocks is retained and indicates that these rocks are "different." This demonstrates one of the strengths of regional geochemistry. Although rocks may look the same, i.e., granitic, they may be geochemically different in their trace element composition, which demonstrates their different geological histories.

As a last example, the regional distribution of selenium in Canadian Prairie hard red spring wheat (*Triticum aestivum* L.) is displayed in Figure 16. These data plotted are averages of the selenium content of harvested grain from 1996 to 1998 (Gawalko et al., 2001). This is an unusual geochemical map, but it represents an important end pause, rather than an end point, in the biogeochemical cycle. In terms of the full biogeochemical cycle involving human populations the next step is milling and incorporation into foodstuffs. Unlike the data for copper, zinc, iron, and manganese, the data for selenium and cadmium show much greater variability (Gawalko et al., 2001). The reason for this variability is that the wheat plants interact with their soil environment to ensure uptake of the essential micronutrients copper, zinc, iron, and manganese. They do not appear to regulate cadmium and selenium that are taken up with the regulated micronutrients to be sequestered in various plant tissues. The spatial distribution of these data is strongly influenced by soil properties, and to a lesser extent the varying selenium content of the soil parent material. The area of highest regional selenium levels is in southwestern Saskatchewan and adjoining Alberta where the soils are dominantly Brown Chernozems (Mollisols, Aridic Borolls), with some Solonchic (Natric) soils. These are relatively organic carbon poor in comparison with the Dark Brown, Black, and Dark Gray Chernozems (Typic, Udic, and Boralfic

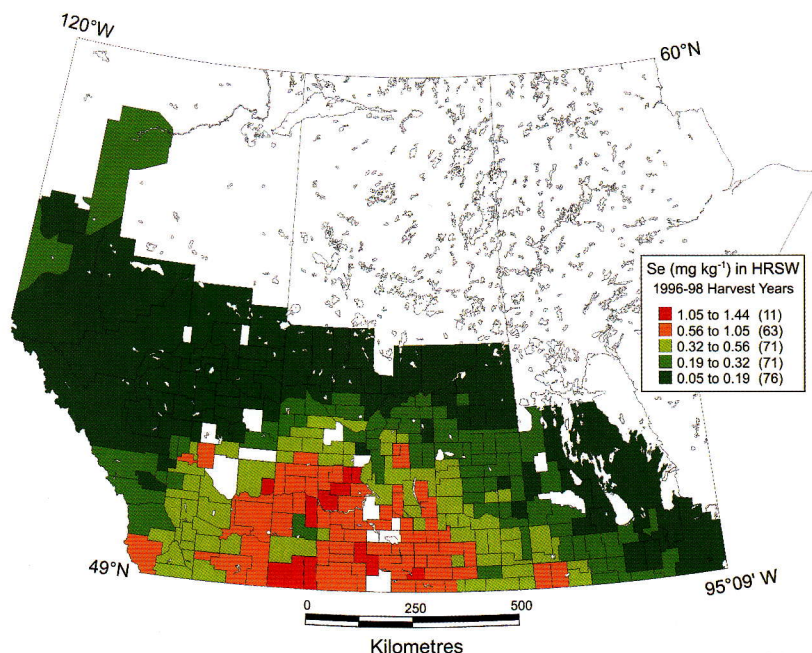


FIGURE 16 Distribution of selenium (mg kg⁻¹) in hard red spring wheat for the 1996–1998 harvests in the Canadian Prairies.

Borolls) and Gray Luvisols (Boralfs) that underlie most of the remainder of the Canadian Prairie agricultural region. Organic compounds in soils form seleno-complexes with labile selenium, thus restricting its availability to the plants. The likely cause of the spatial pattern of high selenium is low organic carbon content. The absence of seleno-complexes favors selenium partitioning into soil pore waters where it is available to the plants. A similar situation has been reported from China (Fordyce et al., 2000; Johnson et al., 2000; Wang and Gao, 2001), where higher soil organic-carbon contents are associated with lower selenium levels in rice and the increased incidence of Keshan disease. Interestingly, a link was made by MacPherson et al. (1997) between the selenium content of Canadian wheat and the selenium status of the Scottish population. The authors related this lowering of selenium status over time to the shift to importing lower selenium European wheat in preference to higher selenium Canadian bread wheat.

The examples above represent the many regional geochemical and biogeochemical studies that have been undertaken in the 20th century. In some cases these data are presented spatially, and in others temporally. They clearly demonstrate the spatial and temporal chemical variability of the natural environment. Life is supported on the Earth's chemically inhomogeneous surface, and there are ecosystem consequences to that reality. To fully understand those consequences and manage any associated risks, a sound knowledge of baseline geochemistry is required.

VI. ESTABLISHING GEOCHEMICAL BASELINES

Applied geochemical surveys are undertaken for one of two basic reasons: (1) to detect geochemical anomalies both natural, e.g., related to mineral occurrences, and anthropogenic, e.g., related to industrial releases; and (2) to map and establish natural background levels or baselines. In the first instance, surveys are designed as search exercises so that a feature of known size and geochemical contrast from the local natural background concentrations can be detected. The sampling is undertaken over an area of fixed extent, perhaps a map sheet, a particular geological terrain, or a particular jurisdiction or economic zone. Where surveys are undertaken to establish natural background and baselines they are

designed to sample the area of interest, a particular jurisdiction or terrain (e.g., an eco-district), in an unbiased manner so that an average may be estimated together with a measure of the data variability. Depending on the size of the area, determining if there is systematic spatial variability across the survey area may be required. The sampling considerations for these two types of survey have been discussed by Garrett (1983).

To be able to reliably estimate the geochemical level and relief (e.g., mean and variance) for a study area a sufficient number of samples must be collected and analyzed. If the study area can be treated as a homogeneous entity, a useful rule of thumb based on the formula for the standard error of the mean ($SE = s.n^{-0.5}$) is that a minimum of 30 sites should be sampled, 60 would be better, and it is probably a waste of resources to sample more than 120. In order to obtain unbiased estimates the samples sites should be distributed randomly across the study area. A common strategy used by geoscientists is to use a square grid with a cell size such that the required number of cells, e.g., a minimum of 30, are present in the study area, and then use a random number generator to locate an x-y position (site) in each cell to be sampled. An alternate strategy is to use prior knowledge of rock or soil type distribution and collect material from sufficient sites from these postulated homogeneous units in an unbiased manner to reliably estimate their geochemical level and relief (e.g., mean and standard deviation). For national-scale surveys many more sites are sampled as the desire is to reveal broad-scale regional geochemical variability.

Clearly, factors such as resource availability influence decisions concerning sample design. Concern is sometimes expressed that widely spaced sampling will not yield reliable estimates. Examples from many parts of the world have demonstrated the ability of low-density sampling to map natural backgrounds on a regional scale, e.g., Darnley et al. (1995), Xie and Cheng (2001), and Reimann et al. (2003). It has to be remembered that if the sampling is unbiased (random) all parts of the study area have an equal opportunity to be sampled, and there is a finite probability that small features that do not form a "significant" proportion of the study area will be missed. If these are important, resources are required to increase the sample density. The cruel reality for surveys is triangular, the apices are survey area, detail of information generated, and resources—time, staff, and funds. One can fix any two of these apices, but one cannot fix all three. To minimize survey costs and maximize the return in information, Xie and Cheng (2001) recommended the widely spaced sampling of major river floodplain sediments. They

demonstrated that sampling densities between 1 site per 1000–6000 km², i.e., about 520 samples representing all of mainland China, can provide reliable estimates of regional background levels. The field work for this survey was completed in one year (1992–1993) by a sampling team of three people. On this basis, they recommend that surveys of this type be completed before more detailed, time-consuming, and expensive surveys are undertaken.

In any baseline survey consistent protocols are essential for both field and laboratory work. The “target population” needs to be specifically defined, e.g., river/stream water collected midstream 10 cm below surface or surface soils collected from 0–25 cm (0–10 inches) at sites at least 100 m from a road that are visibly uncontaminated. Adequate field notes and location (this is now easy with global positioning systems, GPS) information need to be recorded. The procedures for on-site treatment such as filtering and acidification of waters, and storage, shipping, and preparation of samples like drying and screening of soil (2 mm or in the range 0.1–0.18 mm), drainage sediment (in the range 0.1–0.18 mm), and the retention of the fine fraction for analysis need to be clearly laid out. The difference in retained fraction for soils is historical, and care needs to be taken in selecting an appropriate size fraction. Traditionally soil (as prescribed by the United Nations Food and Agriculture Organization, UN-FAO) and environmental scientists have employed the <2 mm fraction for analysis, while applied geochemists have tended to employ a finer fraction of <0.150 or <0.177 mm, as used for drainage sediment surveys in mineral exploration, or <0.063 mm (<63 μm) as used for glacial sediments and the soils developed on them. Compatibility with prior data sets is a major consideration, as are considerations of plant–soil relationships. Appropriate analytical protocols and QA/QC procedures need to be in place. Procedures and considerations for baseline surveys are discussed in Darnley et al. (1995), Salminen and Gregorauskiene (2000), and by the Forum of European Geological Survey (FOREGS) in Salminen et al. (1998).

An important issue to consider in planning baseline surveys is temporal variability. For soils this is not a major consideration; however, for surface and groundwater variations in flow rates resulting from climatic variations such as seasonal rains (e.g., monsoons) or snow-melt events affect the elemental levels observed in the waters. Therefore, care has to be taken to sample a region under similar conditions, and only to subsequently use the data for comparison with data sets collected under similar conditions. In the case of stream

and river sediments, strong seasonal differences in water flow can modify the bed load composition, and therefore its chemistry (Chork, 1977; Rose et al., 1979; Steenfelt & Kunzendorf, 1979). In general, if an effect is present, seasonal rains or spring freshets mass waste bank material into streams and rivers, and fine sediments are then winnowed from the streambed in higher energy (faster flow) environments and deposited in lower energy (slower flow) environments over the period of the subsequent dry season or lower flow period. The result is that levels of trace elements that occur in the finer fraction decrease in higher energy stream environments and increase in lower energy environments. The converse is true for trace elements that occur in coarser or heavier fractions of the sediment. Thus, if seasonal variation is expected, sampling programs should be restricted to longer periods of steady stream flow. If severe weather events occur, e.g., cyclones or hurricanes, the complete bed load may be changed which results in major changes in sediment geochemistry (Ridgway & Dunkley, 1988; Ridgway & Midobatu, 1991; Garrett & Amor, 1994). Thus, if a specific long-term study is undertaken where a knowledge of baseline levels is important, catastrophic weather events will likely require a post-event survey to determine if baseline levels have changed significantly.

Once the analytical data are in hand the accuracy and precision of the data need to be estimated, consistently with international standards (Darnley et al., 1995), to determine if they are adequate. If the field sampling has been structured so that analysis of variance (Garrett, 1983) or geostatistical procedures (e.g., Issaks & Srivastava, 1989) can be applied, the presence of significant spatial trends across the study area can be investigated.

As discussed earlier, geochemical data are often drawn from multiple populations. Therefore it is prudent to summarize the data as percentiles (e.g., minimum, 2nd, 5th, 10th, 25th (first quartile), 50th (median), 75th (3rd quartile), 90th, 95th, 98th percentiles, and maximum), as well as arithmetic means and standard deviations, robust estimates such as the median and mean absolute deviation, and possibly some estimates in logarithmic units. Other properties of the data set to be reported are number of samples analyzed, the lower quantification limit, and how many samples were below the limit. The reporting of the data as percentiles is a nonparametric procedure that avoids any assumption concerning the distribution of the data, and their inspection quickly reveals whether the distribution is skewed. In addition, their availability can assist in setting realistic, in the sense of the natural distri-

bution of an element, regulatory levels as described in Section II.

Often for jurisdictional or regulatory reasons the geographical entities over which baseline surveys are undertaken have no direct, or only an indirect, relation to geology and pedology. The Commission for Environmental Cooperation of the North American Free Trade Agreement (NAFTA-CEC) has prepared a geographic eco-classification for North America (see http://www.cec.org/pubs_info_resources/publications/enviro_conserv/ecomap.cfm and Marshall et al., 1996), which is likely to see increasing use as a way to subdivide natural background data into entities of ecological and environmental relevance. The eco-district

boundaries are strongly influenced by soil (soil series) properties that reflect the underlying geological and biological processes, which in turn reflect climate. An example of presentation of natural background data using this framework is presented in Figure 17 for reverse aqua-regia soluble zinc determined in the $<0.177\text{ mm}$ fraction of stream sediments from the Yukon Territory, Canada. The eco-district medians vary by a factor of 6, again demonstrating the spatial variability in natural background levels. There are sound geological reasons for the spatial patterns: the highest levels relate to zinc-rich black shales in the Selwyn basin in the northeast; low levels relate to the Yukon crystalline terrain in Central Yukon with generally higher

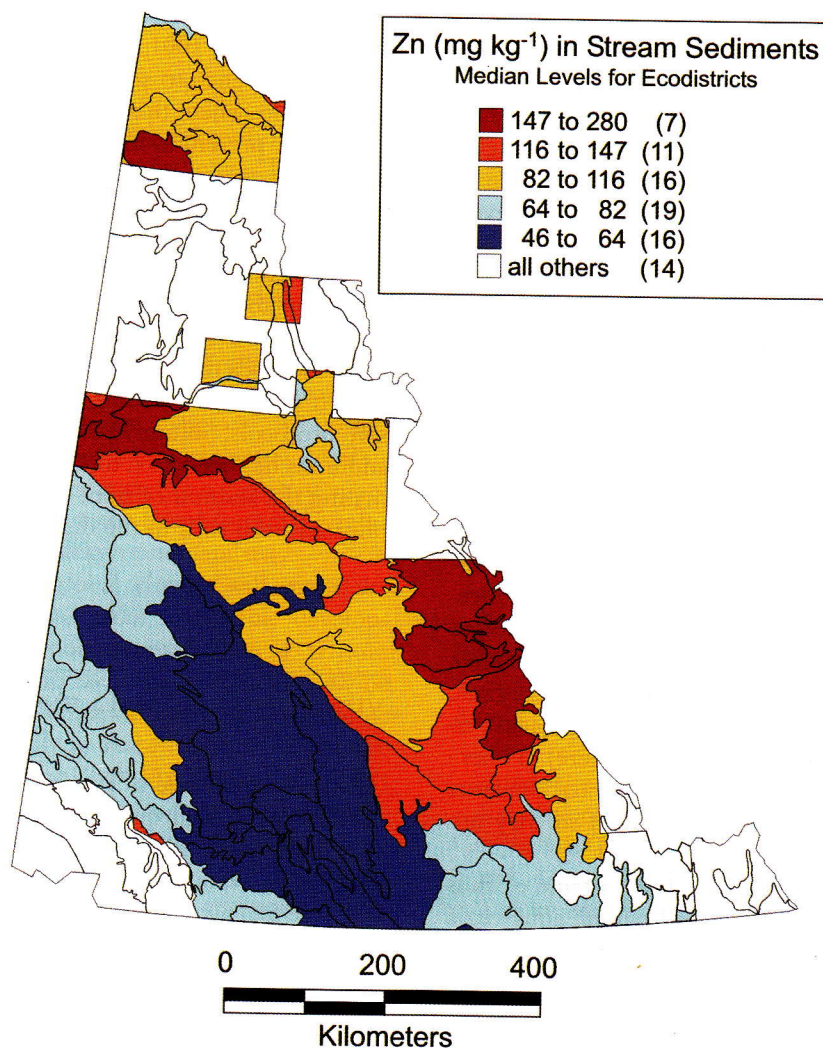


FIGURE 17 Distribution of zinc (mg kg^{-1}) in the $<0.177\text{ }\mu\text{m}$ fraction of 26,862 stream sediments displayed as eco-district median values, Yukon Territory, Canada.

levels to the southwest and northeast; and numerous smaller details may be explained by the presence of particular rock units.

VII. TOTAL ANALYSES AND BIOAVAILABILITY

Geoscientists traditionally determine the total amount of elements in the samples they collect, except for specific geochemical exploration procedures where a wide range of protocols are employed. The total amount of metal in a rock, soil, or sediment is a poor estimator of what may become phyto- or bioavailable and be able to cross cellular barriers.

A wide variety of protocols have been developed by agronomists and ecotoxicologists to better estimate the phyto- and bioavailable amounts of an element in soils, waters, plants, etc. An additional issue is: Bioavailable to what? (Allen, 2002). This has led to a great variety of protocols, some of which are locally adequate for specific studies (see, for example, Sauvé, 2002). However, none is universal, though the estimation of free-ion concentrations in free or pore waters (the Free Ion Activity Model, FIAM) approaches that requirement (see Campbell, 1995). Another important factor influencing the availability of metals in solutions to biota is the presence of dissolved organic carbon compounds, many of which are capable of sequestering trace elements so that they remain unavailable. This situation has been addressed by Tipping (1994) in the WHAM model which includes recognition of humic acid complexes. Finally, it must be remembered that the interaction between the biotic and abiotic realms is not passive. Biota are capable of mediating the passage of ions across cellular barriers. In the case of plants, they are capable of acidifying or releasing low molecular weight organic acids, e.g., phytosiderophores (deoxymugineic acid), to the immediate root environment (rhizosphere) to liberate or chelate micronutrients and other trace elements into the proximal pore waters (moisture) so they are available to the plant.

As a result, much geoscience-driven baseline work is still undertaken using total or near-total aqua-regia or hot nitric acid digestions, and for many sample materials these procedures overestimate the amount of metal that may be available to biota. A notable exception is the recent 1:2,500,000 scale soils found in the geochemical atlas of Poland (Lis & Pasieczna, 1995),

which employed a 1:4 HCl mixture. Although there are sound grounds for this choice, these data are no longer comparable to other international data sets. In an ideal world the best procedure would be to have a total/near-total determination and an appropriate weaker extraction that better estimated the phyto- or bioavailable amount in the sample material. A further point that has to be remembered is that all biota are not created equal, and an extraction that may be good for agricultural crops might be quite inappropriate for soil invertebrates.

The prime controls on phyto- and bioavailability are the mineralogical or material form of an element in question and its mobility in the aqueous environment, e.g., soil or sediment pore waters, fresh stream or lake water, or marine sediments and water. Table IV provides an indication of the mobility of many trace elements of interest as a function of pH and redox conditions (see also Plant et al., 2001, Figure 6).

With reference to solid phases, elements tend to be bioavailable when they are loosely held on mineral surfaces or present as metallo-organic complexes. Thus weak extractants—acetic acid, sodium acetate, calcium chloride, potassium or ammonium nitrate—and chelating agents EDTA, DTPA, and sodium pyrophosphate are commonly used in analytical protocols to estimate phytoavailable amounts of elements in soils. Sauvé (2002) has provided a thorough and extensive review of these methods in the context of determining metal speciation (chemical bonding) in soils. In contrast to the soil protocols, dilute hydrochloric acid with various additions has been used to simulate gastric fluids in estimating the amount of trace elements that could be solubilized from soils in the digestive tract of an animal.

VIII. FUTURE CHALLENGES

The great challenge of the future is to provide consistent, relevant, high-quality geochemical data to support epidemiological research, environmental regulation, and other studies such as agricultural and forestry resource management that concern the transfer of trace elements through potable water and the food chain into human and animal populations.

Attention has been drawn to this by publication of the report on International Geological Correlation Projects 259 and 360 (Darnley et al., 1995) and by Plant et al.

TABLE IV. Mobility of Elements in the Surface Environment

	Oxidizing (pH 5–8)	Oxidizing (pH < 4)	Reducing
Relative mobility			
Highly mobile	Cl, Br, I, S, Rn, He, C, N, Mo, B, Se, Te	Cl, Br, I, S, Rn, He, C, N, B	Cl, Br, I, Rn, He
Moderately mobile	Ca, Na, Mg, Li, F, Zn, Ag, U, V, As, Sb, Sr, Hg	Ca, Na, Mg, Sr, Li, F, Zn, Cd, Hg, Cu, Ag, Co, Ni, U, V, As, Mn, P	Ca, Na, Mg, Li, Sr, Ba, Ra, F, Mn
Slightly mobile	K, Rb, Ba, Mn, Si, Ge, P, Pb, Cu, Ni, Co, Cd, In, Ra, Be, W	K, Rb, Ba, Si, Ge, Ra	K, Rb, Si, P, Fe
Immobile	Fe, Al, Ga, Sc, Ti, Zr, Hf, Th, Sn, REEs, Pt metals, Au, Cr, Nb, Ta, Bi, Cs	Fe, Al, Ga, Sc, Ti, Zr, Hf, Th, Sn, REEs, Pt metals, Au, As, Mo, Se	Fe, Al, Ga, Ti, Zr, Hf, Th, Sn, REEs, Au, Cu, Pt metals, Ag, Pb, Zn, Cd, Hg, Ni, Co, As, Sb, Bi, U, V, Se, Te, Mo, In, Cr, Nb, Ta

After Rose, Hawkes, and Webb, 1979.

(2001). Funding of such regional- and continental-scale mapping activities poses a major challenge. To date significant progress has only been made in China, where there is a national commitment to monitor the surficial environment in sufficient detail to yield useful maps (Xie & Cheng, 2001). Progress has also been made in Europe through the collaborative efforts of nations working through the Forum of European Geological Surveys. The challenge for the future is to create the interdisciplinary teams that can generate the critical mass to organize and execute systematic baseline surveys at continental scales with the support of agencies with the resources and vision to appreciate the value of a global geochemical background database.

The advent of rapid global change will stress the world's resource base, and make sustainable development an even more important issue than it is now. The role of human activity as a causative factor may be argued by some, but it remains that global economic development has radically increased the rate of change in the environment (Fyfe, 1998). As Plant et al. (2001) noted: "The problem is most acute in tropical, equatorial, and desert regions where the surface environment is particularly fragile because of its long history of intense chemical weathering over geological time scales." Change needs to be monitored, but how can it be monitored if the baseline is not known? Concerted international action is required to acquire the data essential for managing the risks that the natural environment poses to the world's population.

SEE ALSO THE FOLLOWING CHAPTER

Chapter 3 (Anthropogenic Sources)

FURTHER READING

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