

GEOCHEMISTRY OF STREAM SEDIMENT FROM THE STATE OF COLORADO USING NURE DATA

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PREVIEW

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COLORADO USING NURE DATA

By

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PREVIEW

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Abstract

The present study used univariate, bivariate, and multivariate statistics together with GIS techniques to investigate the possible abnormal geochemical patterns, or geochemical anomalies in a geochemical data set for Colorado. The elements used on this analyses included twenty four elements are selected which are Al, Ba, Ca, Ce, Co, Cr, Cu, Fe, K, La, Li, Mg, Mn, Na, Nb, Ni, Pb, Sc, Sr, Th, Ti, U, V, and Zn. The study found that the high positive kurtoses show that very high values in the data are rare, may be associated with rare processes such as mineralization. For example Al, Na and K have fairly small kurtoses, showing that these values are more evenly distributed within the data ranges. The spatial distribution of the elements is presented in the forms of five types of maps those were 1) point map of raw data, 2) IDW grid map of the raw data, 3) geologic polygons of the raw data, 4) hydrologic polygons of the raw data, and 5) point map of the outlier values. The geochemistry of the studied element was controlled by the bed rock chemistry with minor anthropogenic sources. The identified physiographic provinces include: 1) Great Plains 2) Rio Grande rift system 3) Rocky Mountains 4) Colorado Plateau and 5) Pionance Basin; their impacts on metal distribution were assessed.

The main factors affecting the distribution and associations of the investigated metals are: a) Factor (1) accounts for 22% of the total variance, and contains a high loading of Al, Co, Cr, Cu, Fe, Mg, Mn, Ni, Sc, Ti, and V, and subdivided into subfamilies, such as the mafic trace elements with the presence of Co, Cr, Fe, Sc, Ni, and V, ultramafic rocks with the presence of Cr, Co, Ni, and Cu, mafic rocks with the presence of Ti, V, and Sc, laterites with the presence of Ni, Cr, and V, b) Factor (2) accounts for 12% of the total variance, and contains a high loading of Ba, Na, and Ti. These elements have high concentrations in felsic igneous rocks, and they may stay in resistate minerals in sediments, c) Factor (3) accounts for 10% of the total variance, and contains a high loading of (Ce, La and U), (Ca and Mg). This group suggests the rare earth element pegmatite type composition with the presence of Ce, La, and U, and carbonate elements with the presence of Ca and Mg, but the Mg and Ca have negative scores. Ca and Mg association is related to naturally occurring carbonate signatures, commonly found in limestones (CaCO_3) and dolomites (Ca/Mg CO_3), d) Factor (4) accounts for 8% of the total variance, and contains a high loading of K and Li. These two elements are the alkali metals in the first group of the periodic table, and e) Factor (5) accounts for 6% of the total variance, and contains a high loading of Pb with a value of 0.93.

The study found that minerals in the lithological units of CMB has incompatible elements (i.e., K, Rb, Sr, Ba, Zr, Th, Rb, Sr, Nd and other rare earth elements that do not easily fit into the crystal lattice structures of mantle minerals such as olivine, pyroxene, spinel, and garnet. Thus weathering product is expected to be depleted in these elements. The study also reported several applications of the investigated dataset and recommended further studies.

Table of Contents

Abstract	iii
Table of Contents.....	iv
List of Tables	vi
List of Figures	vii
1. Introduction.....	1
2. Literature review	4
3. Statement of the Problem and Objectives.....	9
4. Geochemical Families and Related Association.....	11
4.1 Major element of stream sediment.....	12
4.2 Trace element of stream sediment.....	12
4.2.1 Alkali Earths.....	12
4.2.2 First row transition element.....	12
4.2.3 Heavy mineral suite.....	12
4.2.4 Base and toxic metals.....	13
4.2.5 Geochemical Associations.....	13
5. Methodology.....	15
5.1 Data Sources.....	16
5.2 Statistical Analyses.....	20
5.3 Computer Software.....	30
6. Description of Study Area.....	31
6.1 Location and geographic setting.....	31
6.1.1 Physiographic Province	35
6.2 Geological setting	36
7. Univariate Analysis	39
7.1 Element Selection.....	39
7.2 Descriptive Statistics.....	40

7.3 Histograms and Normal Quantile Diagrams	44
7.4 Skewness and Kurtosis	47
8. Bivariate Analysis	55
8.1 Correlation Coefficient.....	55
8.2 Correlation Frequencies	56
8.3 Correlation Scatter Diagrams	57
8.4 Pairwise Correlation.....	57
9. Multivariate Analysis.....	64
9.1 Cluster Analysis.....	64
9.2 Principal Component Analysis.....	66
10. Spatial Analysis.....	68
10.1 Spatial Distribution of the Elements.....	69
11. Discussion.....	76
12. Conclusions.....	80
References.....	83
Appendix.....	87
Curriculum Vita.....	143

List of Tables

Table 4.1: Geologic, Anthropogenic Associations and Signatures	14
Table 7.2: Descriptive Statistics of the Raw Data and Full summary of NURE data (Summary statistics of Box Plot of the raw data, descriptive statistics of the Outliers data, descriptive statistics of the No-Outliers data, as well as Skewness, Kurtosis, and KSL Test are provided digitally in the attached CD).....	40
Table 8.1: Correlation Coefficients between Elements in Stream Sediments in Colorado.....	56
Table 8.2: Pearson product-moment correlation for each pair of variables of the screened NURE data set	59
Table 9.1: Principal Component Loadings from PCA after Rotation for the Maximum Variance.....	67

List of Figures

Figure 5.1: Locations of Stream Sediment Samples from NURE Program (1975-1979)	17
Figure 5.2: Areas of interest for the analyzed elements as observed from Land cover Variations	18
Figure 5.3: Generalized Geological Map of Colorado	19
Figure 5.4: Normal Quantile, Outlier Box, Quantile Box, and Histograms Diagrams	23
Figure 5.5: Definition of the Outlier Box Diagram	24
Figure 6.1: Digital Shaded Relief Map of Colorado with Physiographic Provinces Labels	34
Figure 6.2: Detail geologic map of Colorado Mineral Belt	36
Figure 7.1: Histograms of the Raw Data Set (a normal distribution curve for all the values is superimposed for comparison)	49
Figure 7.2: Normal Quantile Plots for the Raw Data Set	50
Figure 7.3: Histograms of No-Outliers Data Set (a normal distribution curve for all the values is superimposed for comparison)	51
Figure 7.5: Normal Quantile Plots for No-Outliers Data Set	53
Figure 7.6: Normal Quantile Plots for No-Outliers Data after Base of 10 Logarithmic Transformations	54
Figure 7.7: Normal Quantile Plots for Outliers Data Set	55
Figure 8.1: A Portion of Scatter Plot Matrix of the Elements in Stream Sediment in Colorado	58
Figure 9.1: Cluster Tree of Elements Using Cluster Analysis Based on Pearson's Correlation	65

Figure 10.1: Spatial distribution of point map (a) and the IDW grid map (b) of the raw data of Ca. Presentations of the full data in two different layout to ease pattern establishment are presented in Appendix II and III.....	72
Figure 10.2: Geologic (a) and hydrologic (b) polygons of the raw data as well as point map of the outliers (c) values of Ca. Presentations of the full data in two different layout to ease pattern establishment are presented in Appendix II and III.....	73
Fig. 10.3: Geologic and polygons of the raw data of Al and Ba. Presentations of the full data in two different layout to ease pattern establishment are presented in Appendix II and III.....	74
Fig. 10.4 Geologic and polygons of the raw data of Al and Ba. Presentations of the full data in two different layout to ease pattern establishment are presented in Appendix II and III.....	75

1. Introduction

Regional geochemical data provide a means of monitoring the quality of the environment and identifying problem areas. International Union of Geological Sciences and UNESCO (<http://www.unesco.org>) through the International Geological Correlation Program (IGCP) (<http://www.unesco.org/science/earthscience/igcp>) have sponsored the International Geochemical Mapping project.(Darnley,1995). Many aspects of the project were developed specifically for the radioactive elements, with the support of the International Atomic Energy Agency. Changes in the environment cannot be measured without baseline information, and the project has been accepted as a contribution to the International Council of Scientific Union's Global Change Program. The ultimate goal is a systematic global geochemical database, with many applications, including the preparation of the world geochemical atlas.

The behavior or accumulation of elements is influenced by the stability of the minerals, the ability of some minerals to incorporate elements, the adsorption of elements onto clay and hydroxide minerals, mobility of the elements, and other processes. Partition functions, principal component analysis, correlation score coefficients, and descriptive statistics mathematically document the distribution of the chemical elements between the phases. These analyses are evidence of the geochemical associations among elements, which represents mineralogy and chemical interaction of elements. The mobility of elements is also of highly relevant to environmental issues and to questions of the nature of the source, anthropogenic or natural. In essence, this study derives a series of geochemical maps, and statistically analyzed data sets in order to integrate them to geological, chemical and environmental characterizations of the selected area.

This study is based on the use of stream sediment and stream geochemical data collected as part of the National Uranium Resource Evaluation (NURE) program of the U.S. Department of Energy, which are available as U.S. Geological Survey Open-File Report 97-492. This study produced a series of geochemical maps, and statistically analyzed subsets of NURE data, in order to integrate them with geological and environmental characterizations of the study area. The study area covers the entire state of Colorado.

The (NURE) Program in the late 1970s created the first extensive surficial geochemical database for the United States. The database consists of vast amount of chemical data on sediments, soil, and water sampled for the United States in the late 1970s and early 1980s. This component of the NURE program was known as the Hydrogeochemical and Stream Sediment Reconnaissance (HSSR). Stream sediment and stream geochemical data collected as part of the U.S. Department of Energy's NURE Program are available on CD-ROM from the U.S. Geological Survey .That CD-ROM contains technical information concerning types of data collected in the field and obtained by laboratory analysis. Zumlot (2006) indicated that regional surveys have been carried out in some countries, and with increased national and international funding they can be extended to cover the rest of the global land surface of the globe. Many aspects of the project are developed specifically for the radioactive elements, with the support of the International Atomic Energy Agency. However, the geochemistry of stream sediments and their variations are potentially a very useful tool in exploration for mineral deposits as well as in environmental studies, because of the natural chemical plumes which characterize some deposits (Levinson, 1980; Fortescue, 1992).

This study is based on the use of the NURE geochemical database, which is organized into data sets that are arranged by quadrangles of 1×2 degrees. The database of Colorado contains 21,469 records of samples and was initially analyzed. A total of 58 elements were analyzed as will be discussed in the methodology section. The elements selected for the study are: Al, Ba, Ca, Ce, Co, Cr, Cs, Cu, Dy, Eu, Fe, Hf, K, La, Li, Lu, Mg, Mn, Na, Pb, Rb, Sc, Sm, Th, Ti, U, V, Yb, Zn. Some of these elements are categorized as toxic or hazardous substances according to the EPA Toxic Release Inventory (TRI) and the list of hazardous substances from the Agency for Toxic Substances and Disease Registry (ATSDR).

2. Literature Review

Regional mapping of surficial, geochemical data is an important tool in mineral-resource evaluations, geological, agricultural, forestry, and environmental studies (Darnley, 1997; Reid, 2005; Cocker, 1999).

The term ‘geochemical background’ comes originally from the geochemistry associated with the exploration for mineral deposits. Hawkes and Webb (1962) defined background as “the normal abundance of an element in barren earth material” and concluded “it is more realistic to view background as a range rather than an absolute value.” The concept of geochemical background was introduced to differentiate between normal element concentrations and anomalies, which might be indicative of an ore occurrence. Anomaly is defined as a deviation from the norm. A geochemical anomaly, more specifically, is a departure from the geochemical patterns that are normal for a given area or geochemical landscape” (Hawkes and Webb, 1962). To be able to differentiate between background and anomaly, the term threshold was introduced. The threshold is the upper limit of normal background fluctuation.

The U.S. Department of Energy's National Uranium Resource Evaluation (NURE) Program in the late 1970s created the first extensive surficial geochemical database for the United States. Until recently, the NURE database has been largely ignored in the United States. Mapping of the NURE data was facilitated by the need to document the background geochemistry of its major river basins. Because the NURE data were collected in the 1970s, NURE geochemical data provide an important geochemical baseline established prior to the rapid growth that some states has experienced in the 1980s and 1990s.

In environmental geochemistry, there are also problems with the definition of ‘background’. A recent dictionary of environmental science and technology provided the following definition:

“Background concentration of pollutants. If the atmosphere in a particular area is polluted by some substance from a particular local source, then the background level of pollution is that concentration, which would exist without the local source being present. Measurements would then be required to detect how much pollution the local source is responsible for.” Another definition for ‘background’ in environmental sciences is, “the concentration of a substance in a sample material at a distance to a source where the concentration of the substance can no longer be proven to originate from this source” (Porteous, 1996).

Shacklette and Boerngen (1984) collected a suite of 1300 soils across the 48 conterminous states, achieving a 75-km grid sample density of across the country. These were analyzed for 40 elements; modern maps of 20 elements are presented in Gustavsson and others (2001). The low density of these data limits their usefulness for mineral and environmental studies except at very small scales, but they do establish broad trends in elemental concentrations in soils across the country. Koch (1988) prepared a set of large-scale (1:1,785,000) geochemical point maps of Georgia, but these were of limited value because of their generalized nature. Increased availability of the data and significant advances in computer technology and software (i.e., Geographical Information Systems and spreadsheets) permit a more vigorous spatial analysis of the NURE geochemical data. Recently, Carpenter and Carpenter (1991) and Grosz and Schruben (1994) used the NURE data to locate and define heavy mineral deposits in the southeastern United States.

Similarly Cocker (1999) conducted geochemical mapping in Georgia, USA, as a tool for environmental studies, geological and mineral exploration. The Georgia Geological Survey recently used (NURE) program to study stream sediment and stream water geochemical data. Results indicated that bedrock geology and mineralization are the most important variables, that

influence the stream sediment and stream water geochemistry. Anthropogenic sources influence the geochemistry to a lesser and more localized extent.

NURE data were also investigated by other researchers such as Reid (1993) and Cocker (1999). For example Reid (1993) used the (NURE) stream-sediment data to prepare a geochemical atlas of North Carolina, U.S.A. The North Carolina NURE database consists of stream-sediment samples, groundwater samples, and stream-water analyses. The statewide database consists of 6,744 stream-sediment sites, 5,778 groundwater sample sites, and 295 stream-water sites. Neutron activation analyses are provided for U, Br, Cl, F, Mn, Na, Al, V, Dy in groundwater and stream water, and for U, Th, Hf, Ce, Fe, Mn, Na, Sc, Ti, V, Al, Dy, Eu, La, Sm, Yb, and Lu in stream sediments. Supplemental analyses by other techniques are reported on U (extractable), Ag, As, Ba, Be, Ca, Co, Cr, Cu, K, U, Mg, Mo, Nb, Ni, P, Pb, Se, Sn, Sr, W, Y, and Zn for 4,619 stream-sediment samples.

In South Africa, Lombard, Bruin, and Elsenbroek reported in 1999 that they conducted a high-density regional geochemical mapping program since 1973. The results show an excellent correlation between soil chemistry and underlying geological formations. Background values of elements in soils are determined over different lithological units for the identification of anomalous value. Results from geochemical mapping of the Bushveld Complex, South Africa, show a distinct anomaly of platinum and palladium, apparently related to a stratiform platiniferous reef on the boundary between the Main and Upper Zone of the Rustenburg Layered Suite.

Spencer (2003) stated that the Arizona Geological Survey has prepared a map of uranium concentration in Arizona rock and soil using the NURE data. The concentration of uranium and its daughter products in Arizona are highly variable. The 98.3 percent of Arizona's land surface

is made up of rock and soil that have less than 4.5 ppm uranium. In the other 1.7 percent of the state, rock and soil at the surface have uranium concentration greater than 4.5 ppm

Robinson et al., (2004) prepared geochemical maps portraying regional data for pH, alkalinity, and specific conductance for stream waters and a multi-element geochemical dataset for stream sediments collected in the New England states of Connecticut, Maine, Massachusetts, New Hampshire, Rhode Island, and Vermont. A series of interpolation grid maps portray the chemistry of the stream waters and sediments in relation to bedrock geology, lithology, drainage basins, and urban areas. A series of box plots portray the statistical variation of the chemical data grouped by lithology and other features

Ludington et al., (2006) studied the regional distribution of arsenic and 20 other elements in stream-sediment samples in northern Nevada and southeastern Oregon. They used 10261 samples from NURE program in the study area. They analyzed the data using point maps and interpolation between data points to construct high-resolution raster images, which correlated with geographic and geologic information using a geographic information system (GIS).

Recently Zumlot (2006) studied geochemical data for the state of New Mexico consisting of 27,798 stream sediment sites. He investigated twenty-four elements which are Al, Ba, Ca, Ce, Co, Cr, Cu, Fe, K, La, Li, Mg, Mn, Na, Nb, Ni, Pb, Sc, Sr, Th, Ti, U, V, and Zn. Univariate, bivariate, and multivariate statistics and GIS techniques are applied to classify the elements and to identify geochemical signatures, either natural or anthropogenic, with the purpose of finding their sources. The study concluded that (1) the distribution of the elements in stream sediments in New Mexico shows that most of the variability is controlled by the bed rock chemistry. (2) Anthropogenic sources have local influence in the geochemistry of the stream sediments in New Mexico. (3) The mafic factor consists of Co, Cr, Cu, Fe, Ni, Sc, Ti, V and Zn and it also clusters

in the Rio Grande rift and Jemez lineament. (4) The Rare Earth Element(REE) factor consists of Ce, La and U, and it has strong, localized, clusters in the Organ Mountains, Boot Heel, San Andres Mountains and El Capitan Mountains. (5) Mineral exploration and contamination assessment are definitely feasible with the use of the NURE data set and the statistical analyses performed in this study.

As evident from this brief literature review, screening and analysis NURE data has several applications, including identifying and defining: (1) regional and local litho geochemical patterns, (2) regional and local metal anomalies related to known mineral belts and metal deposit occurrences, (3) metal anomalies spatially related to anthropogenic sources, (4) previously unknown mineralization or unidentified contamination. It is the intention of this work to examine the distribution of several representative elements that demonstrate the applications to environmental studies, geological mapping, and mineral exploration in Colorado.

3. Statement of the Problem and Objectives

Human activity has a global impact on the environment, comparable to the effect of geological process. The bedrock geology and mineralization are the most important variables that influence the stream sediment and stream water geochemistry. Anthropogenic sources influence the geochemistry to a lesser and more localized extent (Cocker, 1999). The NURE data were collected in the 1970s, which provided an important geochemical baseline established prior to and during the rapid growth that the western states have experienced in the 1980s and 1990s. The main objective of this study is to produce a series of geochemical maps and statistically analyzed subsets of NURE data for the entire state of Colorado. These maps will be integrated with geological and environmental characterizations of the state of Colorado. Additional objectives include identifying: 1) the anomalous areas of natural or anthropogenic origin; and, 2) the areas of anomalous chemical concentrations, that might be harmful to the health of the populations. This study will also produce a series of geochemical maps, and statistically analyzed sets of NURE data, in order to integrate them with geological and environmental characterizations for Colorado. The specific tasks include:

1. Evaluation of the quality of NURE data.
2. Evaluate natural geochemical variation of sediments in the western U.S; this will be a considerable expansion over previous studies (e.g. Shacklette, H.T., Boerngen, J.G., 1983). This relates to regional background values.
3. Identify the areas of naturally occurring chemically anomalous regions; potentially mineralized areas.
4. Identify areas of chemical anomalies of anthropogenic origin, such as mines or metallurgical plants.

5. Determine of anomalous values for each chemical..
6. Identify geochemical patterns that are related to regional and local geologic units and structures.

PREVIEW

4. Geochemical Groups and Association

Traditionally elements can be classified according to different schemes of classifications that vary upon needs and applications. For example in geochemical applications the Goldschmidt classification is widely used to classify metals into the following groups:

- Lithophile elements: (e.g. Al, B, Ba, Be, Br, Ca, Cr, Cs, K, Li, Mg, Na, Nb, Rb, Sc, Sr, Ta, Th, Ti, U, V, , Zr,) mainly consist of the highly reactive metals of the s- and f-blocks. They also include a small number of reactive nonmetals, and the more reactive metals of the d-block such as titanium, zirconium and vanadium. Their strong affinity for oxygen causes lithophile elements to associate very strongly with silica, forming relatively low-density minerals that thus float to the crust. The more soluble minerals formed by the alkali metals tend to concentrate in seawater or extremely arid regions where they can crystallise. The less soluble lithophile elements are concentrated on ancient continental shields, where all soluble minerals have been weathered.
- Siderophile elements: (e.g. Au, Co, Fe, Mn, Mo, Ni,) These are the high-density transition metals that tend to bond with metallic iron in the solid or molten state. Most siderophile elements have practically no affinity whatsoever for oxygen. They form stronger bonds with carbon or sulfur, but even these are not strong enough to separate out with the chalcophile elements. Manganese and molybdenum do form strong bonds with oxygen but in the free state (as they existed on the primitive earth when free oxygen did not exist) can mix so easily with iron that they do not concentrate in the siliceous crust as do true lithophile elements. However, ores of manganese are found in much the same sites as are those of aluminium and titanium owing to manganese's great reactivity towards oxygen. Because they are so concentrated in the dense core, siderophile elements are known for their rarity in the Earth's crust.
- Chalcophile elements (e.g. Ag, As, Bi, Cd, Cu,, Pb, , Zn). Those metals (sometimes called "poor metals") and heavier nonmetals that have a low affinity for oxygen and prefer to bond with sulfur as highly insoluble sulfides. Because these sulfides are much denser than the silicate minerals formed by lithophile elements, chalcophile elements

separated below the lithophiles at the time of the first crystallization of the Earth's crust. This has led to their depletion in the Earth's crust relative to their solar abundances, though because the minerals they form are nonmetallic, this depletion has not reached the levels found with siderophile elements. They not likely to be depleted on Earth as a whole relative to their solar abundances since they do not form volatile hydrides. Zinc and gallium are somewhat "lithophile" in nature because they often occur in silicate or related minerals and form quite strong bonds with oxygen. Gallium, notably, is sourced mainly from bauxite.

However, the following classification is the most relevant to the objectives of this research.

4.1 MAJOR ELEMENT CHEMISTRY OF MAJOR MINERALS IN STREAM SEDIMENT

(e.g. Al, Ca, Fe, K, Mg, Na, Ti)

The depositional setting of stream sediments strongly influences the mineralogy of the sediments and the concentrations of major elements. High (Al) concentration is associated with clay and silt-rich sediments. Na and K concentrations are high over areas of granites, reflecting the influence of feldspar, and micas. Ca and Mg are high over areas of carbonate rocks reflecting the influence of soluble carbonate and calcsilicate minerals.

4.2 TRACE ELEMENTS OF STREAM SEDIMENT

4.2.1 Alkali Earths (e.g. Ba, Sr)

Elevated concentrations generally occur in stream sediments associated with intermediate to mafic igneous rocks.

4.2.2 Transition Elements (e.g. Sc, V)

Elevated concentrations of Sc and V occur in stream sediments associated with mafic rocks. Chemical variation in Sc and V is similar to variation in Fe.

4.2.3 Heavy Mineral Suite (e.g. REE, Th, Ti, U, Ce)

Elevated concentrations of REE (Ce, La), Th, and U occur in silt- and sand stream sediments enriched in the heavy-mineral suite of monazite (light REE, Th, U), and related minerals, such as xenotime (heavy REE). Monazite is resistant to weathering and is concentrated in the silt-sized heavy mineral fraction of stream sediments. Contributing sources of monazite to stream sediments include high-metamorphic-grade clastic metasedimentary rocks and REE-rich granites (Robinson et al., 2004).

4.2.4 Base Metals (e.g. Cu, Zn, Pb)

The base metals Cu, Pb, Zn tend to be associated with Fe-Mn-hydroxide minerals in stream sediments. Natural sources of base metals to stream sediments include weathered sulfide minerals, oxides and silicate minerals, and mafic rocks. Anthropogenic sources of base metals (Cu, Pb, Zn) are related to industrial sites and automobile traffic.

4.2.5 GEOCHEMICAL ASSOCIATIONS

Table 4.1 shows some geochemical associations and signatures reported in the literatures. Statistical clusters or associations of elements can be compared to geological and or anthropogenic signatures found in the environment.

TABLE 1 GEOLOGIC AND ANTHROPOGENIC ASSOCIATION AND SIGNATURES

Elements	Signature	Source	References
Cu, Pb, Zn	Geologic	Hydrothermal Deposits	(Levinson, 1974)
Cu, Pb, Zn, Cr, Mn	Anthropogenic	Mining, Milling and Smelting	
Co, Cr, V, Ni, Fe, Sc	Geologic	Mafic Rocks	(Levinson, 1974, Thorton, 1983)
Ca, Mg	Geologic	Carbonate Rocks	
Na, K, Al	Geologic	Felsic Majors	(Levinson, 1974)
Ce, La	Geologic	Alkalic felsic igneous rocks	
Cr, Ni	Anthropogenic	Plating operation	