21A.

APPLICATION OF HYDROGEOCHEMISTRY TO THE SEARCH FOR BASE METALS

W.R. Miller
U.S. Geological Survey, Denver, Colorado

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Abstract

As the world's exposed mineral deposits become depleted, new techniques need to be developed to aid in the search for buried deposits. If circulating water comes into contact with mineralization at or below the surface, and particularly within the zone of oxidation, certain elements may concentrate above the natural background and form aqueous dispersion halos. The detection and interpretation of these halos form the basis of hydrogeochemical prospecting.

The behaviour of trace components in water that is in contact with mineralization depends on the type of mineralization, the enclosing rocks, and the chemical and hydrological environments. In addition, the geochemical and physical environment will affect the mobility of trace elements. Factors that determine the formation and shape of aqueous dispersion halos include: (1) the physical and chemical properties of the migration forms of the elements; (2) the composition of the mineralization; (3) climate; (4) topography; (5) composition and permeability of the formation containing or covering the mineralization; (6) direction of groundwater flow; and (7) geologic environment including structure.

Interpretation of hydrochemical data includes both the treatment of single variables and the use of multivariate techniques. The treatment of single variables consists of the plotting of the concentrations of those pathfinder elements that should occur with the expected type of mineralization and that should be mobile for the given chemical and physical environment. The use of multivariate techniques allows more sophisticated interpretation of water analyses, particularly pattern-recognition techniques. Water chemistry used in conjunction with thermodynamic data can also be used to interpret the geochemical data and to gain a better understanding of the geochemical cycles of selected elements in the weathering environment.

Résumé

Etant donné que les gisements connus de minéraux à travers le monde s'épuisent rapidement, il faut mettre au point de nouvelles techniques afin de faciliter la recherche de gisements souterrains. Lorsque l'eau d'érosion vient en contact avec une minéralisation à la surface ou en profondeur, en particulier à l'intérieur de la zone d'oxydation, certains éléments peuvent se concentrer au-dessus du fond naturel et former des auréoles de dispersion aqueuse. La détection et l'interprétation de ces auréoles constitue la base de la prospection hydrogéochimique.

Le comportement des composantes à l'état de trace dans l'eau qui est en contact avec la minéralisation dépend du type de minéralisation, des roches encaissantes et des milieux chimique et hydrologique. De plus, le milieu géochimique et physique influe sur la mobilité des éléments à l'état de trace. Les facteurs qui déterminent la formation et le modelé des auréoles de dispersion aqueuse comprennent: 1) les propriétés physiques et chimiques des formes de migration des éléments; 2) la composition de la minéralisation; 3) le climat; 4) la topographie; 5) la composition et la perméabilité de la formation contenant ou recouvrant la minéralisation; 6) la direction de l'écoulement des eaux souterraines, et 7) le milieu géologique, y compris la structure.

L'interprétation des données hydrogéochimiques comprend à la fois le traitement des variables simples et l'utilisation de techniques multi-variables. Le traitement des variables simples consiste en l'enregistrement graphique des concentrations d'éléments des indicateurs minéraux qui peuvent exister dans le type de minéralisation prévu et qui seraient mobiles pour le milieu chimique et physique donné. L'utilisation de techniques multivariables permet une interprétation plus poussée des analyses de l'eau; c'est le cas des techniques permettant d'en confirmer la composition. La chimie de l'eau, utilisée conjointement avec des données thermodynamiques, peut aussi être utilisée pour l'interprétation de données géochimiques, de façon à permettre une meilleure compréhension des cycles géochimiques des éléments choisis dans le milieu d'actions météoriques.

INTRODUCTION

Water is called the "universal solvent". All natural substances will dissolve in water to some measurable extent, given proper circumstances and time. Therefore the waters of an area will have a certain natural background concentration for various elements. In addition, water is capable of penetrating below the earth's surface to depths as great as 2 km and dissolving natural substances. Some of this solute-containing water will eventually return to the surface and become part of the natural water system of an area. The water chemistry will depend on the source and history of the water. If the water has come into contact with mineralization at or below the surface, and particularly if within the zone of oxidation, certain elements will increase in concentration above the natural background and form geochemical dispersion halos. The detection and interpretation of these aqueous-dispersion halos form the basis for hydrogeochemical prospecting.

Types of samples used for hydrogeochemical prospecting are waters from springs and seeps; groundwater from wells; surface waters from streams, rivers, and lakes; snow; and groundwater from drillholes and mine workings.

The advantages of using water as a sampling medium for geochemical exploration are: 1) water is capable of penetrating below the earth's surface, and providing a third dimension in the search for hidden ore deposits; 2) water is usually a homogeneous and representative sample of the watershed; 3) water requires no sample preparation except for filtering and acidifying; 4) elements in water under oxidizing conditions, generally form large dispersion halos; 5) water is particularly adapted to the detection of large low-grade deposits; and 6) water is involved with most low temperature-pressure geochemical processes and can be useful in the interpretation of other geochemical data.

Unfortunately, because water is usually moving and in a dynamic state, the aqueous dispersion halos associated with mineralization can be affected by changes through time, such as those caused by rainfall or season. Disadvantages of hydrogeochemical prospecting therefore include the following: 1) changes through time occur in the water chemistry at the sampling point, owing to variability in discharge of the water or fluctuations of the chemical contents of water with season and rainfall; 2) analyses of trace components in water can be difficult, time-consuming, and expensive in the low ranges (µg/L); 3) sources of water may not be present for the needed sampling density; and 4) low concentrations of trace components in water are susceptible to contamination and storage problems.

Because of these disadvantages, hydrogeochemical prospecting for base metals with few exceptions has not been used to any general extent outside of the Soviet Union. However recent advances in both analytical techniques and data interpretation have reduced or eliminated many of these disadvantages.

DISCUSSION

Generally, trace elements in water can be used as pathfinders for mineralization. A trace element can be defined as normally occurring in water in concentrations less than 0.1 mg/L. Sources for trace elements in water are usually the enclosing rocks and soils, but other sources, such as pollution, are possible. The migration of trace elements in water depends on both intrinsic and extrinsic factors of migration. Intrinsic factors depend on the structure of the electron shell of the atom, and an example of this is the complexing capacity of an element. Extrinsic factors depend on the geochemical environment; for example, copper, lead, and zinc are more mobile in an acid environment, whereas molybdenum and arsenic are more mobile in an alkaline environment.

The behaviour of trace components in water that is in contact with mineralization depends on the type of mineralization, the enclosing rocks (the chemical activity of the rocks or their physical nature such as fracturing), and the chemical and hydrological environments. The chemical reactions that control the trace element concentrations in water include solution, precipitation, and adsorption. The mechanisms for migration of elements in water include ionic, complexing, colloidal, sorption, suspension, and electrochemical.

SAMPLING AND ANALYTICAL METHODS

Natural water is a continuously changing medium. The manner in which water is collected is more important than with most other media; collection must be performed carefully and consistently. Clean, acid-rinsed plastic bottles should be used for collection. Before sampling, the bottle should be rinsed several times with the water to be sampled. Wells should be allowed to flow prior to sampling. Turbid water should be filtered using a 0.45 µm membrane filter. To insure a consistent method, it is a good technique to filter all samples that are to be analyzed for trace elements. Filtering removes the large colloids and sediments which upon addition of acid may contribute to contamination (Kennedy et al., 1974).

The sample that is to be analyzed for trace elements should be acidified to pH<2 with metal-free nitric or hydrochloric acid.

Storage of samples before analyses should be in a cool place out of exposure to the sun to minimize growth of algae. If this is not possible, chloroform should be added to retard algal growth.

On-site determinations for reconnaissance exploration purposes are usually kept to a minimum, but may include determinations of pH or conductivity. For detailed exploration or orientation studies, additional field determinations may be needed. Possible determinations include: 1) temperature; 2) flow rate; 3) pH; 4) redox potential; 5) dissolved gases such as O_2, CO_2, and H_2S; 6) conductivity; 7) specific components such as Fe^{+2} and HCO_3^-.

For dilute waters, pH can generally be satisfactorily determined at the end of the day by the use of potentiometer at the campsite or motel. For more accurate pH measurements, a potentiometer can be used to measure pH in the field.

On-site descriptions will differ depending on the purpose of the survey. Possible on-site descriptions include: 1) sample source; 2) width and depth; 3) turbulence or the degree of aeration; 4) presence of suspended or organic material; 5) presence of precipitates, moss or algae; 6) local bedrock geology; 7) dominant vegetation; 8) elevation and geographic location in relation to the watershed; and 9) possible contaminants. In addition to the above, when sampling water wells, the following should be included: 1) water well configuration, tanks, pressure system; 2) depth of well and aquifers; 3) hydrological information; and 4) owner's address.

Recent advances in equipment and techniques allow methods that have sufficient sensitivities for trace-element analyses. Some of the methods that are used for trace-element analysis are shown on Table 21A.1.

An atomic adsorption unit coupled with a resistively heated device is capable of the sensitivities needed for many trace-element analyses. This method is probably the most useful one at the present time. Emission spectrometry using a plasma source and ion chromatography have come into use and will probably become more important in the near future.

METHODS

The geochemical and physical environment will affect the mobility of trace elements. Factors that determine the formation and shape of aqueous dispersion halos include: 1) the physical and chemical properties of the migration forms of the elements; 2) the composition of the mineralization; 3) climate; 4) topography; 5) composition and permeability of the formation containing or covering the mineralization; 6) direction of groundwater flow; and 7) geological environment including structural setting.

During intense oxidation of an ore deposit, an increase of 100 times above background in associated trace components is not unusual. Under reducing conditions, the contrast of most trace components will be less than under oxidizing conditions. Table 21A.2 lists the most frequently

Contents

Table 21A.1

Some analytical methods used for analysis of trace elements in water

Methods	Comments
Atomic absorption spectrometry	Trace metals usually concentrated by solvent extraction techniques.
Atomic absorption spectrometry/ resistively heated devices	Usually no prior concentration, provides good sensitivity and at the present time it is probably the best methods for trace metal analyses.
Emission spectrometry (DC-Arc)	Multielement analyses, sample must be concentrated by evaporation, precipitation, or other means.
Emission spectrometry (Induction coupled plasma)	Multielement analyses, potentially one of the better methods.
Anodic stripping voltammetry	Means for differentiating metal species.
Ion chromatography	Multielement analysis, mostly anions.
Colorimetric or spectrophotometric	Usually slow.
Fluorimetric	U analysis, usually slow.
Ion selective electrodes	Poor sensitivity except for F^-.
Neutron activation analysis	Sensitive method but expensive.

Table 21A.2

The most frequently encountered and maximum contents (in ppb) around mineralization of a number of microcomponents in neutral waters of the supergene zone (after Shvartsev et al., 1975)

Element	Most frequently encountered contents (regional background)		Maximum contents found	Contrast ratio
	Waters of oxidizing setting	Waters of gley setting		
Barium	2.0 - 10	2.0 - 2.5	500	400
Beryllium	0.1 - 0.8	0.05 - 0.3	300	3 000
Boron	10 - 50	-	20 000	2 000
Bromine	20 - 200	-	20 000	1 000
Vanadium	0.5 - 2.0	0.5 - 1.5	90	180
Tungsten	0.1 - 0.5	-	200	2 000
Iodine	1 - 10	-	5 000	5 000
Cadmium	0.1 - 0.5	0.05 - 0.5	260	5 200
Cobalt	0.5 - 3	0.2 - 10	68	340
Lithium	5 - 10	-	10 000	2 000
Manganese	10 - 50	20 -400	15 000	1 500
Copper	2 - 8	1 - 5	1 000	1 000
Molybdenum	1 - 5	0.2 - 3	8 000	40 000
Arsenic	1 - 5	0.1 - 2.0	100	1 000
Nickel	0.8 - 5	0.5 - 2	200	400
Tin	0.1 - 0.5	0.1 - 0.5	60	600
Mercury	0.5 - 3.0	-	20	40
Lead	1 - 8	0.5 - 4	250	500
Selenium	0.5 - 1.0	-	50	100
Silver	0.1 - 0.6	0.05 - 0.5	50	1 000
Strontium	5 - 50	3 - 20	1 000	300
Antimony	1 - 10	0.5 - 5.0	1 300	2 600
Uranium	0.5 - 5	0.3 - 3.0	500	1 700
Fluorine	50 -1 000	-	11 500	230
Chromiun	5 - 10	0.1 - 5	600	6 000
Zinc	5 - 50	2 - 20	2 500	1 250

encountered trace-element concentrations in water. The physical environment also influences the mobility of trace components in water. Hydrogeochemical prospecting in different physical environments requires different approaches. A summary for hydrogeochemical prospecting in different environments is shown in Table 21A.3.

The types of expected mineralization also need to be considered in the selection of pathfinder elements for hydrogeochemical prospecting. Examples are the selection of copper, lead, sulphate, and zinc to detect polymetallic mineralization, or the selection of molybdenum and copper to detect porphyry-metal-type mineralization. Pathfinder elements associated with different types of mineralization are shown in Table 21A.4.

INTERPRETATION

Interpretation of hydrogeochemical data includes both the treatment of single variables and the use of multivariate techniques. The treatment of single variables consists of the plotting of the concentrations of those pathfinder elements that should occur with the expected type of mineralization and that should be mobile for the given chemical and physical environment. Several pathfinders are usually selected. Ratios such as Cu/Zn or Pb/Zn can be useful (since zinc is more mobile than copper or lead, the ratio will usually increase toward mineralization). Corrections for changes through time due to rainfall or season can sometimes be made by normalizing the pathfinder elements with conductivity or components such as chloride or sodium that are little affected by chemical controls in water. In a similar manner, other effects on the water chemistry can be detected and sometimes corrected. Examples of maps (Miller and Ficklin, 1976) using a single variable of a study conducted in the White River National Forest, Colorado are shown in Figure 21A.1. An intense copper anomaly occurs along Cataract Creek where the concentration of copper in water reaches 480 µg/L. A less intense copper anomaly is also present west of Hunter Peak. A zinc anomaly, which coincides with the copper anomaly, also occurs along Cataract Creek. Concentrations of zinc in water reach 35 µg/L. In addition an intense molybdenum anomaly, where the concentrations of molybdenum reach 450 µg/L, occurs west of Hunter Peak. The results indicate two main areas of interest, the area along Cataract Creek and the area west of Hunter Peak.

Just as recent advances in equipment and techniques have allowed the more effective use of water for geochemical prospecting, recent use of mathematical and statistical methods has allowed more sophisticated interpretation of water analyses.

Because the main purpose of a geochemical survey is to detect anomalous areas, pattern-recognition techniques are advantageous. An example of the use of this type of technique (Miller and Ficklin, 1976) is an extended form of Q-mode factor analysis and is shown in Figure 21A.2; which uses the same data as Figure 21A.1. A five-factor model explains 96 per cent of the total variation. Three factors are interpreted as being related to the mineralization. The first factor is represented by loadings on calcium and sulphate and is interpreted as reflecting pervasive pyrite

Contents

Table 21A.3

A summary for the application of hydrogeochemical prospecting in different environments

	Areas of permafrost	Areas of arid conditions	Areas of swamps	Areas of mountainous terrain
Characterization of water	Geochemical movement is partly electrochemical, with water in the active zone above the permafrost gradually becoming enriched in trace components.	High values for pH and salinity and slightly high background values for many trace elements but with low contrast.	Low pH values and flow rates and slightly high background values for many trace elements but with low contrast.	Chemically aggressive waters. The maximum contrast is obtained for moderate relief and rainfall; higher relief or rainfall tends to decrease contrast.
Mobility of elements	Mineralized bodies that emerge at the surface usually have oxidation zones and high contrast (difference between anomalous and background values); dispersion patterns traceable in the active zone by both surface and spring waters.	Fair to moderate mobility of many elements because of flat landscape and lack of chemically aggressive waters. Elements capable of forming negatively-charged ions or soluble compounds are the most mobile such as U, Mo, V, As, and Se.	Movement and precipitation of chemical elements are governed mainly by the concentration, pH, and contents of humic and fulvic acids, and organic material in contact with the water.	Good mobility of many elements because of the aggressive waters, the greater relief, and the more likely chance for oxidizing conditions.
Optimum time for sampling	Either the first part or the the last part of the summer.	When the number of springs and ephemeral streams will be the greatest, usually in the spring and fall.	Most times except during runoff or flooded periods.	Usually after spring runoff when the streams have returned to normal flow or during low streamflow, which is usually during the fall and winter.
Abundance of possible sample sites	Good sample density is possible for both spring and surface waters.	Fair to poor sampling density, usually ephemeral streams and some springs	Abundant water, good sampling density.	Usually abundant water with good sampling density for both spring and surface waters. First-order streams and springs are probably the best source for water samples.
General comments	Chemical weathering reduced because of cold temperatures, organic material is abundant.	There is an accumulation of salts and secondary minerals and the lack of organic material.	Dispersion patterns of mineralization may be characterized by a set of elements which may not correspond exactly to their paragenic associations in the mineralization. Dispersion patterns are reduced because of little dissection and less favourable mobility under more reducing conditions and abundant organics.	The dissection of terrain increases the possibilities for the intersection of mineralization and oxidizing conditions.

Contents

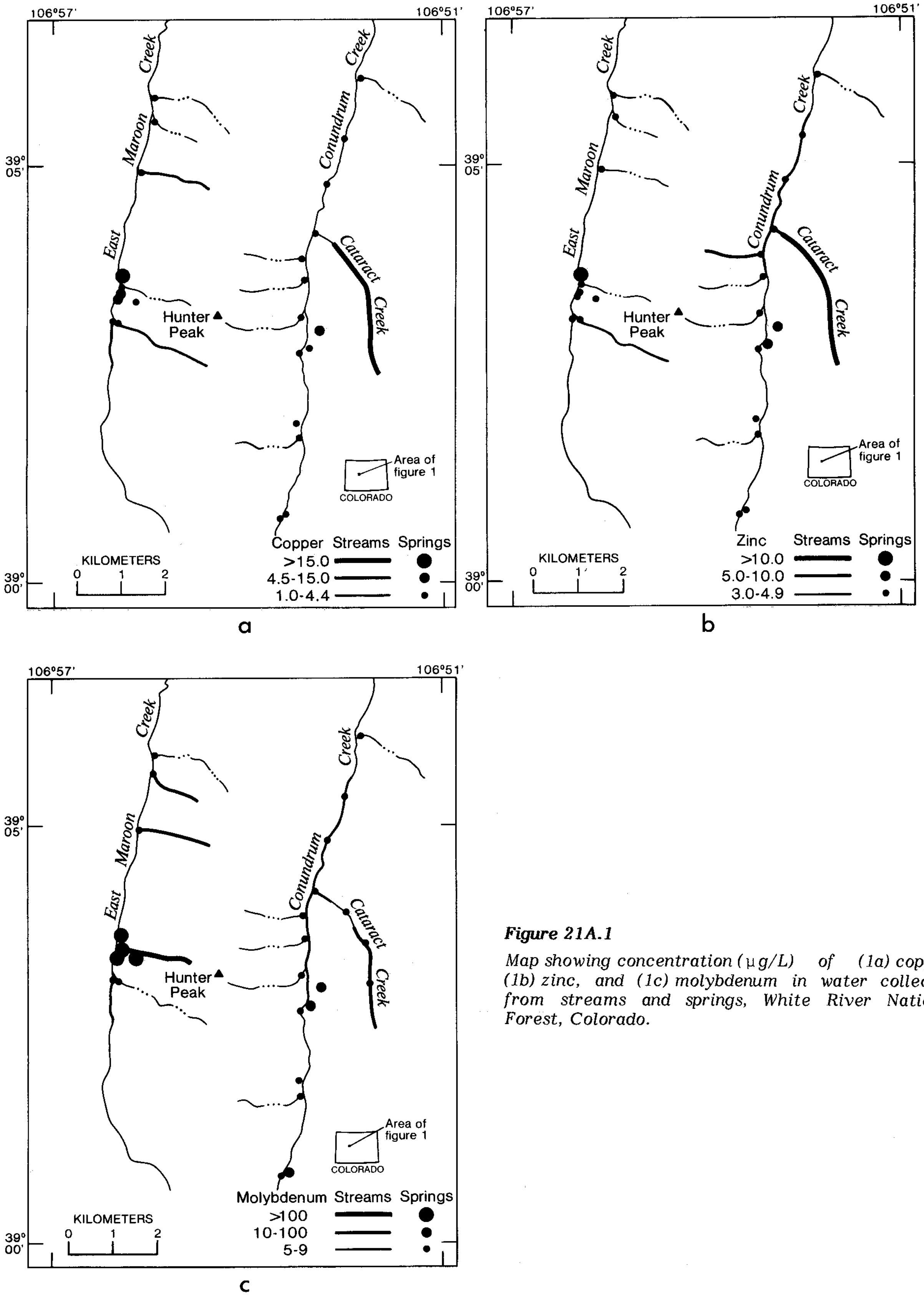

Figure 21A.1

Map showing concentration ($\mu g/L$) of (1a) copper, (1b) zinc, and (1c) molybdenum in water collected from streams and springs, White River National Forest, Colorado.

Contents

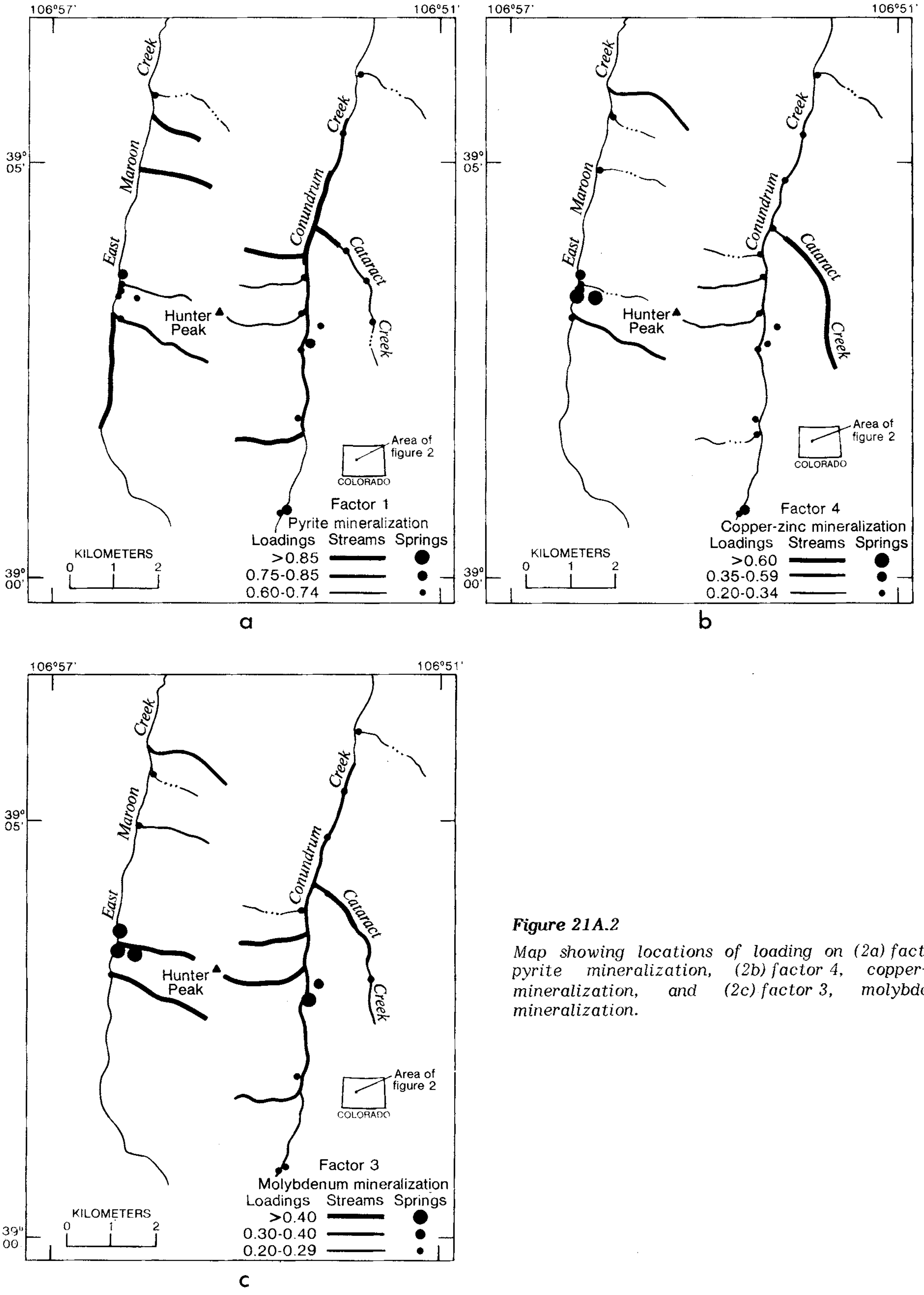

Figure 21A.2

Map showing locations of loading on (2a) factor 1, pyrite mineralization, (2b) factor 4, copper-zinc mineralization, and (2c) factor 3, molybdenum mineralization.

Contents

Table 21A.4

Hydrogeochemical indicator elements for different types of deposits (after Beus and Grigorian, 1975).

Type of deposit	Indicator elements of orebodies	
	Strongly oxidizing	Weakly oxidizing
Copper-pyrite	Cu, Zn, Pb, As, Ni, Co, F, Cd, Se, Ge, Au, Ag, Sb	Zn, Pb, Mo, As, Ge, Se, F
Polymetallic	Pb, Zn, Cu, As, Mo, Ni, Ag, Cd, Sb, Se, Ge	Pb, Zn, As, Mo, Ni
Molybdenum	Mo, W, Pb, Cu, Zn, Be, F, Co, Ni, Mn	Mo, Pb, Zn, F, As, Li
Tungsten-beryllium	W, Mo, Zn, Cu, As, F, Li, Be, Rb	W, Mo, F, Li
Mercury-antimony	Hg, Sb, As, Zn, F, B, Se, Cu	Ag, As, Zn, B, F
Gold ore	Au, Ag, Sb, As, Mo, Se, Pb, Cu, Zn, Ni, Co	Ag, Sb, As, Mo, Zn
Tin ore	Sn, Nb, Pb, Cu, Zn, Li, F, Be	Sn, Li, F, Be, Zn
Titaniferous magnetite	Ti, Fe, Ni, Co, Cr	Ni, Fe
Spodumene	Li, Rb, Cs, Mn, Pb, Nb, Sr, F, Ga	Li, Rb, Cs, F
Copper-nickel	Ni, Cu, Zn, Co, Ag, Ba, Sn, Pb, U	Ni, Zn, Ag, Sn, Ba
Beryllium-fluorite	Be, F, Li, Rb, W	Be, F, Li
Baritic-polymetallic	Ba, Sr, Cu, Zn, Pb, As, Mo	Be, Sr, As, Mo

mineralization. The weathering of pyrite releases sulphate and hydrogen ions to the natural waters of the area. The hydrogen ions are then exchanged for calcium ions during the chemical attack of rock minerals, particularly plagioclase and calcite, which are abundant in the area, and this exchange is reflected in the water chemistry. The first factor generally affects waters in the area surrounding Hunter Peak.

Factor 4 (Fig. 21A.2) is interpreted as reflecting copper-zinc mineralization and is represented by loadings on copper, zinc, hydrogen ion, fluoride, and sulphate. This factor shows up strongly in waters along Cataract Creek, in a manner similar to copper and zinc as shown in Figure 21A.1, but factor 4 also shows a general zoning pattern around Hunter Peak, usually within and partly coinciding with the pyrite mineralization factor.

Factor 3 (Fig. 21A.2) is interpreted as reflecting molybdenum mineralization and is represented by loadings of molybdenum, potassium, silica, fluoride, and bicarbonate. The area showing the largest influence by this factor centres around Hunter Peak. Two streams draining the east side of Hunter Peak have only background concentrations of molybdenum (Fig. 21A.1), but loadings for factor 3 for waters of these two streams are anomalous showing the advantage of this technique in detecting patterns. The zoning – with the molybdenum mineralization pattern in the centre, surrounded by the copper-zinc mineralization pattern, and this in turn surrounded by a pyrite mineralization pattern – is interpreted as a possible porphyry molybdenum deposit. In addition a second area of interest is indicated along Cataract Creek and is interpreted as representing hydrothermal vein-type mineralization. A major mineral exploration company is now using this method to explore for molybdenum mineralization in Colorado.

Trend surface analysis, regression analysis, cluster analysis, and weighted sums are a few of many multivariate techniques available for use for interpretation.

The use of thermodynamic data in making equilibrium calculations or the construction of stability diagrams may also prove helpful for interpretation even though organo-metallic reactions are not taken into account. Equilibrium calculations are useful in predicting the forms of migrations of elements in natural waters within given limits for Eh, pH, and activities of aqueous species. The discovery of water with near-equilibrium concentrations of trace metals with respect to corresponding secondary minerals is a good indication of mineralization.

SUMMARY

Conclusions for the application of hydrogeochemical prospecting are: 1) waters collected from first-order streams, springs, and wells are probably the best hydrogeochemical media; 2) when selecting associated and indicator elements for a hydrogeochemical survey, it is important to take into account types of mineralization that may be present and the physical and chemical environment; 3) hydrogeochemical surveys should be carried out within short periods of time to reduce temporal effects; 4) in humid areas low-water level is usually the best time to sample, in arid areas the best time to sample is when the number of springs producing water is at a maximum; 5) false anomalies may be distinguished by using the water chemistry; false anomalies usually have a less-varied suite of trace elements; 6) water is capable of penetrating below the earth's surface and detecting hidden mineralization; and 7) hydrogeochemical prospecting is most effective when combined with other media and methods to obtain maximum information. An example of effective combination of media for geochemical exploration would be the combined use of water and heavy-mineral concentrates as geochemical sampling media. This would be an effective means of obtaining maximum geochemical information because both secondary and primary dispersion patterns may be detected.

Reports on hydrogeochemical prospecting are appearing with more frequency in the literature: an excellent review of hydrogeochemical methods used in the Canadian Shield was given by Boyle et al. (1971). In addition a list of papers (available in English) on hydrogeochemical prospecting for base metals during the last ten years appears in the Selected Bibliography. As those deposits that are easily discovered by conventional methods are gradually exhausted, new methods will become increasingly important. Research needed to make the technique more useful in the future include: 1) improved analytical techniques particularly multielement methods; 2) a better understanding of geochemical cycles in different environments, particularly for lesser-studied elements such as Sn and W; 3) a better understanding of chemical changes in water due to seasonal and rainfall effects; 4) a better understanding of the role of organo-metallic complexes; and 5) the use of interstitial water as a geochemical sampling medium. In addition, a better union between hydrogeochemistry and hydrology is needed to better understand the role of water in the subsurface environment. Although much work remains to be done, hydrogeochemical prospecting will undoubtedly become more important during the next ten years.

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Contents