Chapter

Geochemistry Applied to the Exploration of Mineral Deposits

John Luis Manrique Carreño

Abstract

Geochemistry can be applied to the exploration of mineral deposits, for which it is necessary to understand the fundamentals of geochemical prospecting, the geochemical dispersion of elements based on their chemical properties. This chapter presents the basics of geochemical prospecting including: element mobility depending on ionic potential, pH, and Eh, with examples of Cu mobility during supergenic alteration of a primary sulfide deposit, a brief overview of sampling/geochemical prospecting methods, as well as a case study of the geochemical prospecting study carried out in the vanadium (V), uranium (U), and zinc (Zn) sedimentary mineral deposit of Puyango, Ecuador, in which anomalous and subanomalous values were detected in rock samples of various pathfinder elements of V and U.

Keywords: geochemical prospecting, mineral deposits, ionic potential, mobility, redox

1. Introduction

Geochemical prospecting is the earth science that applies the theoretical knowledge of geochemistry with the aim of being able to locate mineral deposits, through the study of the primary and secondary dispersion of the elements, performing studies of lithogeochemistry, stream sediments, surface water, soil, and other methods [1, 2].

This chapter shows a review of the basic concepts of geochemical prospecting, taking as an example the mobility of copper (Cu) in during supergenic alteration of a primary sulfide deposit, depending on the ionic potential (charge/radius ratio of the ion), the hydrogen potential (pH), and the redox potential (Eh) [1, 2]. It also includes a brief description of methods (soils, lithogeochemistry, stream sediments, hydrogeochemistry), as well as the case study of geochemical prospecting carried out, in a sedimentary mineral deposit, in Puyango, Ecuador. In this study, anomalous and subanomalous values of several pathfinder elements of vanadium (V) and uranium (U) mineral deposits were detected, among which the following stand out: phosphorus ($P_2O_5 > 5.12$ wt.%), nickel (Ni > 1824 ppm) and, yttrium (Y > 219 ppm), among the most important and subanomalies of barium (Ba > 1459 ppm) and lead (Pb > 32 ppm).
2. Mineral deposits

Mineral deposit is a mineralization (referring to an area of the crust where ores were deposited) of sufficient size and grade (concentration), which under favorable circumstances could be exploited with economic benefits, which has sufficient reserves [3].

The concentration of the metals in the deposits varies widely in a range of few parts per million (1–100 g/t or ppm) in noble metals such as platinum (Pt), palladium (Pd), gold (Au), silver (Ag), at a low percentage (1–10 wt.%) for Cu, zinc (Zn), lead (Pb), and higher grade or tenor (40–60 wt.%) for aluminum (Al), chromium (Cr), iron (Fe), and aggregates.

Mineral deposits can be classified from the genetic point of view into five main types: 1) deposits of magmatic segregation ((chromites, iron-titanium-vanadium (Fe-Ti-V), nickel-copper (Ni-Cu) sulfides, platinum group elements (PGEs), diamonds, carbonatites)), 2) pegmatite deposits (( tin-niobium-tantalum (Sn-Nb-Ta), uranium-thorium (U-Th), lithium (Li), rare earth elements (REE)), 3) hydrothermal deposits (volcanogenic massive sulfurs Cu-Zn-Pb, SEDEX Ag-Pb-Zn, Mississippi Valley type (MVT) Ag-Pb-Zn, epithermal Au-Ag, copper-molybdenum-gold (Cu-Mo-Au) porphyry, 4) metamorphic deposits (polymetallic Skarn, graphite), 5) sedimentary deposits ((placers, laterites, Banded Iron Formations (BIFs), Li brines, U in sandstones, among others)) [3, 4].

3. Geochemical prospecting fundamentals

It is mainly concerned with studying the enrichment or impoverishment of certain chemical elements in the vicinity of mineral deposits [5]. Geochemical prospecting is done by systematic measurements of one or more chemical parameters, usually at trace concentrations, of naturally occurring materials in the Earth’s crust. The types of samples that are collected include rocks, soils, gossan, river or lake sediments, groundwater, surface water, steam or gases, and vegetation [5] (Figure 1).

Primary geochemical dispersion mainly affects the migration of elements of economic interest due to processes, such as the formation and crystallization of magmas and hydrothermal activity. At the local level, these processes can lead to an enrichment or impoverishment of the elements, generating geochemical anomalies [1, 5].

Halos are enriched or depleted in various elements as a result of introduction or redistribution related to mineralization formation phenomena. The shape and size of the halo are exceptionally variable due to the various mobility characteristics of the elements in solution and microstructures in the rocks [1, 2].

The redistribution of chemical elements on or near the Earth’s surface due to weathering, transport, sedimentation, and/or biological activity is classified as secondary geochemical dispersion. The secondary geochemical dispersion halo comprises the dispersed remnants of mineralization, caused by surface processes of chemical and physical weathering and the redistribution of the primary patterns. The halo can be recognized in samples taken from soil, rocks, sediments, vegetation, groundwater, and volatiles, at a distance of meters to tens of kilometers [2].

“Pathfinder” or “indicator or tracer” elements (Table 1) are characteristic parameters in geochemical prospecting. These are relatively mobile elements due to the physical-chemical conditions of the solutions in which they are found [1].
The ionic potential is the charge/radius ionic ratio, which together with the pH and Eh allows us to understand the mobility of chemical elements during geochemical dispersion, being important parameters for geochemical prospecting [1, 2]. Ions with

![Image of samples collected: rock, soil, and surface water (source: author).](Image)

**Figure 1.**
Types of samples collected: rock, soil, and surface water (source: author).

<table>
<thead>
<tr>
<th>Mineral deposit</th>
<th>Metals/elements of economic interest</th>
<th>Pathfinders</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chromium Orthomagmatic (stratiform)</td>
<td>Cr</td>
<td>Cr, PGE, High Mg</td>
</tr>
<tr>
<td>PGE Orthomagmatic (stratiform mafic-ultramafic)</td>
<td>PGE (Pt, Pd, Ru, Re, Os)</td>
<td>PGE, Cu, Ni, Cr, Ti, High Mg</td>
</tr>
<tr>
<td>REE in Carbonatite</td>
<td>REE, Nb</td>
<td>Th, U, Ti, Zn, Nb, Y, Ce, Mo, Cu, V, P, Mn, S, La, Pb, Zr, Ba</td>
</tr>
<tr>
<td>Porphyry Copper</td>
<td>Cu, Mo, Au</td>
<td>Cu, Mo, Au, Ag, W, B, Sr, High S</td>
</tr>
<tr>
<td>VMS</td>
<td>Cu, Zn, Pb</td>
<td>Cu, Zn, Co, Ag, Ni, Cr</td>
</tr>
<tr>
<td>Epithermal Gold</td>
<td>Au, Ag, Cu</td>
<td>Au, As, Sb, Hg, Ag, Pb, Zn</td>
</tr>
<tr>
<td>SEDEX Zn-Pb</td>
<td>Zn, Pb</td>
<td>Cu, Pb, Zn, Ba</td>
</tr>
<tr>
<td>Sandstones Uranium</td>
<td>U</td>
<td>U, V, Mo, Se</td>
</tr>
<tr>
<td>Lateritic Nickel</td>
<td>Ni, Sc or Co (by-product)</td>
<td>Ni, Co, Cr</td>
</tr>
</tbody>
</table>

**Table 1.**
Examples of pathfinders in some types of mineral deposits.

The ionic potential is the charge/radius ionic ratio, which together with the pH and Eh allows us to understand the mobility of chemical elements during geochemical dispersion, being important parameters for geochemical prospecting [1, 2]. Ions with
ionic potential less than 3 can be soluble in water, for example: alkaline cations (Li⁺, Na⁺, K⁺), alkaline earth cations (Ca²⁺, Mg²⁺), transition metal cations (Fe²⁺, Cu²⁺, Cd²⁺, Zn²⁺, Pb²⁺). Ions with an ionic potential between 3 and 12 will be insoluble under certain pH conditions, examples: Fe³⁺, Al³⁺, Si⁴⁺, Zr⁴⁺, Pb⁴⁺, REE³⁺, Th⁴⁺, Nb⁵⁺. Ions with ionic potential greater than 12 will form soluble cations or anions, examples: P⁵⁺ (phosphate), As⁵⁺, S⁶⁺ (sulfate), Se⁶⁺, U⁶⁺ (uranyl), Mo⁶⁺.

An example of secondary geochemical dispersion can occur due to Cu sulfide weathering and erosion, in which surface waters percolate to primary sulfide deposits, oxidizing many ores and producing solvents that dissolve other minerals. The chemical reaction observed below describes the oxidation process of chalcopyrite (Cu ore) in waters rich in oxygen and carbon dioxide, producing goethite (gossan), Cu²⁺ (in solution), sulfate, sulfuric acid, and carbonic acid [3, 5]:

\[
\text{CuFeS}_2 + O_2 + H_2O + CO_2 \rightarrow \text{Fe(OH)}_3 + \text{Cu}^{2+} + \text{SO}_4^{2-} + \text{H}_2\text{SO}_4 + \text{H}_2\text{CO}_3 \quad (1)
\]

Cu²⁺ in oxidizing environments and with acidic pH (< 4) is a soluble cation; therefore, it can be leached from the mineral deposit in surface waters and underground waters. If the pH is higher, various secondary minerals can be formed such as: chalcocite (CuSO₄), azurite (Cu₃(CO₃)₂(OH)₂), malachite (Cu₂(CO₃)(OH)₂), including tenorite (CuO) at alkaline pH. This process is known as supergenic sulfide alteration and may be useful in geochemical prospecting for Cu sulfide mineral deposits [3, 4].

3.1 Geochemical anomalies

The purpose of geochemical prospecting studies is to find geochemical anomalies, which are abnormal chemical patterns in a region. For this, the background values, threshold, subanomalies, and anomalies must be established, which are statistically calculated from the data. The “background” values are characterized by the normal range of concentration of elements in regional perspective rather than localized mineral occurrences. It is significant to establish the background value of the area against anomalies due to the accumulation of economic minerals, if any, they can be identified [1, 5].

The arithmetic mean (average) is obviously skewed by some high scattered values. The most frequent value (median) tends to be within the relatively narrow range and is considered to represent the normal or background abundance for that particular element in that area.

The “threshold” (Eq. (2)) value is defined as the probable upper limit or lower limit of the background value, at some statistically precise confidence level. Any sample that exceeds this threshold is considered possibly abnormal and belongs to a separate population. The following equation is usually used to calculate it:

\[
\text{Threshold} = \text{Background (median)} + \text{standard deviation} \quad (2)
\]

The subanomaly is calculated using the background + twice the standard deviation, while the anomalies are calculated with the background plus three times the standard deviation.

4. Geochemical prospecting methods

In general terms, they can be classified into the following types depending on the sampling stages, the nature of the terrain, the signal associated with the
mineralization, the type of analytical instrumentation available, and finally, the time and cost allowable for the program [5]:

- Pedogeochemistry (soil sampling).
- Lithogeochemistry (rock sampling).
- Sampling of fluvial sediments.
- Sampling of heavy minerals.
- Hydrogeochemical sampling.
- Geochemistry of radiogenic isotopes.
- Geochemical sampling of glacial sediments.
- Vegetation sampling.
- Gas sampling.

Some of the afore mentioned methods are described below:

### 4.1 Soil sampling

Soil is the unconsolidated product of weathering. It is usually found at or near its source of formation such as residual soils. It can be transported over long distances, forming alluvial soils. It is widely used in geochemical prospecting and often produces successful results.

Anomalous element enrichment from underlying mineralization may occur due to secondary dispersion in overlying soil, weathered product, and groundwater during weathering and leaching processes. The dispersion of the elements can be large, forming an exploration target larger than the actual size of the deposit.

### 4.2 Lithogeochemistry

Rock sampling is useful during regional work to recognize favorable geochemical provinces and favorable host rocks to host mineral deposits. Most of the epigenetic and syngenetic mineral deposits show primary dispersion around the mineralization, due to the presence of abnormally high values of the trace elements.

Lithogeochemistry aims to identify primary dispersion, diagnosis of other geochemical characteristics, and association of trace elements, which are different in sterile rocks.

Rock outcrop can be sampled directly by breaking up a small hand sample using a geological hammer or hammer and chisel. Generally, 1–3 kg is a suitable sample size (mass). Sampling is based on the analysis of fresh rocks or individual minerals. Sampling is conducted on a uniform grid across a geologic terrain that includes various rock types from fresh outcrops, wall rocks, and core samples.

### 4.3 Sampling of fluvial sediments

River sediment sampling is the most widely used in all reconnaissance and detailed study of watersheds. Many minerals, particularly sulfide minerals, are unstable in the weathering environment, breaking down as a result of oxidation and other chemical reactions. The process will produce secondary dispersion of both minerals and trace elements. Elements will move in solid form and in solution greater relative distances within the basin drainage.
The mobility of different elements will vary significantly, between fine-grained particles and, eventually, in detrital rock fragments, clay minerals, organic and inorganic colloids enriched in ore minerals, and in pathfinders, which are deposited downstream.

The optimum size fraction varies in different environments, and generally 80 mesh size is recommended. Samples are generally collected in natural sediment traps along streams.

4.4 Hydrogeochemical sampling

There are two types of water sources, i.e., groundwater and surface water; they have very different chemical and physical properties. Groundwater is produced in springs and wells. It has a better potential in geochemical prospecting especially if it is acidic (low pH) by dissolving and transporting metallic elements such as Cu, Pb, Zn, Mo, Sn, S, U, Ni, and Co more than in surface waters, due to chemical weathering and oxidation followed by leaching.

Surface water from streams, rivers, and oceans has less dissolving power, and fine-grained sediments absorb much of the metals carried by the water. River water samples and sediment samples are collected simultaneously for analysis.

Water samples are easy to obtain. About a liter of water is collected and stored in a special container. Metal solubility decreases with increasing pH 4–7. Therefore, the pH is recorded at the time of sampling and other physicochemical parameters (Eh, temperature, salinity, total dissolved solids, among others). Suspended solids are filtered before analysis.

5. Case of study: U, V, Zn sedimentary mineral deposit of Puyango, Ecuador

Here, the outcome of a preliminary study on the geochemical prospecting of a set of rock samples of the Puyango sedimentary deposit in Ecuador is presented, focusing on the quantification of certain trace elements in whole rock samples. Analytical techniques such as X-ray fluorescence and inductively coupled plasma mass spectrometry were used. The chemical obtained data were used to determinate and quantify the concentrations for the majority and some particularly economic trace chemical elements such as U, V, and Zn.

5.1 Geology of Puyango sedimentary deposit

The study area is a part of the Alamor—Lancones basin [6] and is located between the Amotape Tahuín Block of Paleozoic age to the west and the Celica continental volcanic arc to the east [7]. This Late Cretaceous basin is of marine origin, composed of a turbiditic sequence, whose siliciclastic sediments were supplied from the west, and the vulcanoclastic sediments were supplied from the east [8]. The Chirimoyo and Guineo micro-watersheds are geologically located in the Early Cretaceous Ciano, Zapotillo, and Cazaderos (Figure 2) sedimentary formations initially identified as belonging to the Alamor group [9], but later detailed studies in the Cazaderos Formation have differentiated the sequences from various sedimentary environments, identified informally, such as Bosque de Piedra and Puyango Formations [8]. At present, they are identified according to the outcropping site as Quebrada Los Zábalos Unit.
and Puyango Unit (Figure 2), maintaining the Zapotillo and Ciano Formations identified in the first instance [10].

Rocks of Paleozoic age initially identified as Metamorphic Series Tahuín by Kennerley (1973) [9], now defined as Amotape—Tahuín Block, within which the Tahuín Semipelitic Division [11] comprises the informal units, El Tigre and La Victoria. The El Tigre unit is exposed to the north of the study area characterized by sedimentary rocks and low-grade metamorphic sequences, with immature medium-grain sandstones (La Victoria unit) interbedded with fissile shales of brown color and meta-sandstone from fine-grained.

The Early Cretaceous sedimentary rocks are formed by the Quebrada los Zábalos unit that lies to the north, overlying discordant contact with the El Tigre unit. It is constituted by basal layers of silicified fine-grained sandstones, thick conglomerates with subangular clasts of metamorphic composition and volcanic, coarse volcanic sandstones, very compact fine sandstones containing incrusted fossil trunks, and volcanoclastic middle sandstones containing outcrop fossil trunks [10]. The Puyango Unit occupies a strip of E-W direction. The rocks of this unit are chemical sediments made of black limestones and bituminous limestones interspersed with calcareous sandstones. The Puyango Unit (Figure 2) through paleontological interpretations is attributed to early to late Albian age [12, 13]. It is considered that the Puyango unit is of a platform environment below the wave train allowing the deposition of calcium carbonate in an anoxic environment, the sandstones are interpreted as distal turbidites. The Unit is found discordantly to the Quebrada Los Zábalos Unit. The unit is strongly deformed, and the erosion of the Pre-Campanian makes it difficult to determine its thickness (approximately 300 m) [10].
Late Cretaceous rocks are attributed to the Ciano Units made up of fine-grained sandstones, limonites, and shales. The Zapotillo Unit that overlies the Ciano Unit is made up of black shales and grawacas, flysh type. The Cazaderos Unit is found discordantly to the calcareous rocks of the Puyango unit to the north and south to the rocks of the Ciano and Zapotillo units, while in the eastern part, they discordantly cover the metamorphic rocks of the El Tigre unit. The unit consists of brown, medium-grained sandstones, black shales interspersed with siltstones, and is attributed to an environment of turbiditic forearc sequences due to its fossiliferous content [8], indicating this faunal association of a late Campanian to Maastrichtian age.

5.2 Method

Rock samples were collected in outcrops, approximately 1 kg of fresh material per sample, 30 samples in were taken in Puyango sector, Ecuador, some rock replicas were taken for internal verification. The samples were dried at 105 °C for 24 hours in the oven, then they were cut, crushed, and pulverized. The chemical analyses were made in Actlabs, Canada, carried out using the analytical package: Code 4LITHO, Major Elements Fusion ICP(WRA)/Trace Elements Fusion ICP/MS(WRA4B2), detecting the following elements (with its detection limits or lower limits): Si (0.01 wt.%), Al (0.01 wt.%), Fe (0.01 wt.%), Mn (0.01 wt.%), Mg (0.01 wt.%), Ca (0.01 wt.%), Na (0.01 wt.%), K (0.01 wt.%), Ti (0.01 wt.%), P (0.01 wt.%), Zr (2 ppm), Sr (2 ppm), Cr (20 ppm), Ba (2 ppm), Y (1 ppm), Rb (2 ppm), Ni (20 ppm), Zn (30 ppm), Pb (5 ppm), V (5 ppm), U (1 ppm), and Th (1 ppm). XRF was used for internal verification of samples, using the USGS reference material code SGR-1b (Green River Shale), in the Laboratory of Analytical Geochemistry of the Department of Geosciences of the Universidad Técnica Particular de Loja, Ecuador.

5.3 Results

The statistical parameters were calculated: minimum, maximum, mean, median, and standard deviation (Table 2), according to which black bituminous limestones have the mean U content of 27 ppm, reaching the maximum value of 266 ppm (Figure 3b), while the mean content of Ni is 331 ppm, reaching the maximum value of 2937 ppm. As for V and Zn, the mean values are 1897 ppm V and 1048 ppm Zn, with maximum values of 6837 and 4704 ppm, respectively (Figure 3a). The content of another element of economic interest, yttrium (Y), widely ranges, reaching the maximum value of 257 ppm (Figure 3b).

To calculate the background value, the median of the values was used, for the threshold the median + standard deviation was used, for the values of subanomalies the median + twice the standard deviation was used and, finally, to calculate the anomalies, the median + three times the standard deviation (Table 3).

5.4 Final considerations

The calculations in the dataset in rock samples of Puyango sector, Ecuador, identify anomalies of U (>158 ppm), V (>6440 ppm), Zn (>3959 ppm), P2O5 (>5.12 wt.%), Ni (>1824 ppm), and Y (>219 ppm), among the most important and subanomalies of Ba (>1459 ppm) and Pb (>32 ppm). All of these elements are pathfinders for U in sedimentary mineral deposits.
<table>
<thead>
<tr>
<th>Element</th>
<th>Min</th>
<th>Max</th>
<th>Mean</th>
<th>Median</th>
<th>Stand Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂ (wt.%)</td>
<td>7.27</td>
<td>60.19</td>
<td>20.75</td>
<td>15.97</td>
<td>13.72</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>0.69</td>
<td>21.13</td>
<td>4.65</td>
<td>2.95</td>
<td>5.30</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.23</td>
<td>9.23</td>
<td>2.03</td>
<td>1.22</td>
<td>2.48</td>
</tr>
<tr>
<td>MnO</td>
<td>0.01</td>
<td>0.09</td>
<td>0.02</td>
<td>0.01</td>
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<tr>
<td>MgO</td>
<td>0.38</td>
<td>1.51</td>
<td>0.69</td>
<td>0.63</td>
<td>0.27</td>
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<tr>
<td>CaO</td>
<td>0.76</td>
<td>49.77</td>
<td>37.38</td>
<td>41.53</td>
<td>12.98</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.04</td>
<td>1.05</td>
<td>0.24</td>
<td>0.21</td>
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<td>K₂O</td>
<td>0.17</td>
<td>3.05</td>
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<td>0.75</td>
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<tr>
<td>TiO₂</td>
<td>0.07</td>
<td>0.95</td>
<td>0.27</td>
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<tr>
<td>P₂O₅</td>
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<td>5.92</td>
<td>1.23</td>
<td>0.43</td>
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<td>LOI**</td>
<td>6.05</td>
<td>40.62</td>
<td>31.23</td>
<td>32.82</td>
<td>9.11</td>
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<tr>
<td>Zr (ppm)</td>
<td>3</td>
<td>234</td>
<td>99</td>
<td>40</td>
<td>62</td>
</tr>
<tr>
<td>Sr</td>
<td>121</td>
<td>1528</td>
<td>877</td>
<td>963</td>
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<tr>
<td>Cr</td>
<td>20</td>
<td>586</td>
<td>184</td>
<td>174</td>
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<tr>
<td>Ba</td>
<td>4</td>
<td>1612</td>
<td>670</td>
<td>620</td>
<td>420</td>
</tr>
<tr>
<td>Y</td>
<td>14</td>
<td>257</td>
<td>63</td>
<td>51</td>
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<tr>
<td>Rb</td>
<td>7</td>
<td>152</td>
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<td>Ni</td>
<td>29</td>
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<td>331</td>
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<tr>
<td>Zn</td>
<td>58</td>
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<td>1048</td>
<td>713</td>
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<td>Pb</td>
<td>5</td>
<td>40</td>
<td>17</td>
<td>15</td>
<td>9</td>
</tr>
<tr>
<td>V</td>
<td>123</td>
<td>6837</td>
<td>1897</td>
<td>1538</td>
<td>1634</td>
</tr>
<tr>
<td>U</td>
<td>1</td>
<td>266</td>
<td>27</td>
<td>8</td>
<td>50</td>
</tr>
<tr>
<td>Th</td>
<td>1</td>
<td>17</td>
<td>4</td>
<td>2</td>
<td>6</td>
</tr>
</tbody>
</table>

*Min: minimum; Max: maximum; Mean: Median; Standard Deviation in wt.% (SiO₂ to LOI) and in ppm (trace elements).
**% Loss on ignition at 1000°C.

Table 2.
Statistical parameters of the chemical composition of the Puyango deposit rocks.
6. Conclusions

Geochemical prospecting is an important tool in the early stages of exploration of mineral deposits, since it allows delimiting anomalous areas that could be favorable for the discovery of a mineral deposit of economic interest.

To carry out a geochemical prospecting study, it is necessary to know the geochemical fundamentals that control the mobility of the different elements: ionic potential (charge/radius ratio of the ions, physicochemical parameters such as Eh and pH, among others).

When a mineral deposit is formed, some elements (pathfinders) will be dispersed to a greater extent, which can be used as tracers of the deposit.

Data from a case study of geochemical prospecting of the sedimentary mineral deposit of V, U, and Zn from Puyango, Ecuador, in which anomalous and
subanomalous values of several pathfinder elements associated with elements of eco-
nomic interest were detected, among which stand out: P₂O₅ (>5.12 wt.%), Ni (>1824 ppm), and Y (>219 ppm), among the most important and subanomalies of Ba (>1459 ppm) and Pb (>32 ppm).

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