STREAM-SEDIMENT GEOCHEMISTRY OF PUERTO RICO, ISLA DE VIEQUES, AND ISLA DE CULEBRA

By

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GEOCHEMISTRY OF PUERTO RICO

INTRODUCTION

A regional stream-sediment geochemical survey of the Commonwealth of Puerto Rico began in the early 1970's as an outgrowth of the cooperative exploration geochemical studies by the Department of Natural Resources of Puerto Rico (DNR) and the United States Geological Survey (USGS) on the Río Tanamá and Río Viví copper deposits. From the early 1970's through the mid 1980's stream-sediment sampling continued over a large part of the island. In 1980 a cooperative project between the DNR and the USGS was started to continue the regional stream-sediment sampling program, and this project continued for several years. A total of 2,493 stream-sediment samples were collected during this phase of the project.

In 1990 a systematic search of USGS computer records and records in the DNR chemistry laboratory yielded a geochemical data set for the stream sediments that indicated that the regional geochemical sample net for the island was incomplete. In 1991 we made two field trips to Puerto Rico and an additional 292 stream-sediment samples were collected and analyzed in order to complete the regional geochemical survey.

The total number of stream-sediment samples used in this report is 2,785. Because of the lengthy period of time between the original stream-sediment survey and the survey completed in 1991, and because analytical techniques and procedures have changed somewhat over the years, the two resulting geochemical data sets have generally been kept separate for interpretive and statistical purposes. The two data sets are referred to as the "old" and the "new" in this report. All geochemical data from the regional stream-sediment geochemical surveys are published in USGS Open-File Reports 92-353A and 92-353B (Marsh, 1992) and are included in appendix D.

Sample collection and processing

During the cooperative project between the DNR and the USGS, stream-sediment samples were taken from first-order streams that drained basins from less than 1 square kilometer to as much as 3 square kilometers. Most of the sediment samples were collected from the main channel of active streams. Due to time and budget constraints the sediment samples collected in 1991 were from first- and second-order streams and represented drainage basins as large as 10 square kilometers. These samples were also collected from the main channel of active streams.

Sediment samples were screened through a 2-mm-mesh stainless-steel screen in the field, and a 4 X 6-in. sample bag of the resulting material was collected for further processing. The samples were air dried and sieved through a 250-m (U.S. Standard Sieve #60 mesh) stainless-steel sieve for the "old" samples and through a 177-m (U.S. Standard Sieve #80 mesh) stainless steel sieve for the "new" samples. The -250-m and -177-m fractions respectively were then pulverized for analysis.

Contamination

Due to the high population density on the island of Puerto Rico, most of the streams sampled for the regional geochemical survey were contaminated in some manner. Contamination ranged from refuse from nearby habitation to large objects such as car bodies, refrigerators, construction materials, and such. The results of the geochemical survey do not seem to reflect any abnormal anomalies at the 1:200,000 scale of these maps that can be directly attributable to contamination. It is possible, however, that at larger scales, where the details of individual streams would be shown, some single-point anomalies might prove to be the result of contamination.

<u>Statistical methods</u>

Univariate statistics, correlation coefficient tables, cumulative frequency plots, factor analysis, factor-score plots, and single-element distribution plots were used to evaluate the stream-sediment geochemical data. The geochemical data were examined and basic statistics were generated for both the "old" and the "new" data (table 1; table 2). From the basic statistics, cumulative frequency plots (figs. 1-22) were generated for the 11 elements utilized in the geochemical interpretation in this report for the "old" and "new" data.

For the purposes of this study, geochemical values in the 90th percentile or above (figs. 1-22) were considered to be anomalous. For most of the 11 elements plotted, the 90th percentile was well above the crustal abundance for the individual elements (table 3).

Some of the lower detection limits of the semiquantitative spectrographic data for individual elements are above crustal abundances, making the analyses less useful for interpretation. Because of this, the only reported values for some elements (such as gold silver, and zinc) are in the highly anomalous range. When an element has a very restricted number of valid determinations that represent only a small part of the distribution, the data is considered to be highly "censored." For the Puerto Rico geochemical data sets, any elements that had less than 38-43 percent valid determinations were considered to be censored.

Although statistically somewhat difficult to deal with, many of these highly "censored" data are important in the interpretation of the geochemistry, especially in determining suites of elements related to mineralization. When using this highly "censored" data, as in the case of gold and silver, any reported value is usually at or above the 90th percentile of the distribution and was considered anomalous for this interpretation.

Correlation - In addition to the above statistics, tables of correlation coefficients were generated (table 4; table 5). These tables show three different things; (1) correlations between elements, (2) the standard deviation for each element, and (3) the number of samples involved in making the correlation. Correlations are shown in the upper half of the tables. Those in **bold** and **<u>bold shaded</u>** typeface are statistically significant and correlate at the 99 percent confidence level (99 percent of the time the correlation is significant and not the result of a random event) for the elements shown. The correlations indicate lithogeochemical associations as well as associations related to mineralization. The number of samples involved in each correlation is shown in the lower half of the tables. The standard deviations for each element are shown in the middle of the tables. To read the tables, find the element of interest (either vertically or horizontally), move across or down to the other element of interest and note the number. If you are in the upper half of the table the number will be the correlation coefficient and if you are in the lower half of the table the number will be the number of samples involved in the correlation calculation. If you look at the same element along both the vertical and horizontal axes, the resulting number will be the standard deviation for that element (shown in UNDERLINE typeface).

Multivariate analysis

Analysis of multivariate data allows consideration of changes in several properties simultaneously. Multivariate analysis used in geologic studies includes multiple regression, discriminate functions, cluster analysis, and factor analysis. Factor analysis is a method for identifying common factors (or, in the case of the Puerto Rico geochemical data, suites of elements) in the variables of a data set and is useful in interpretation when the number of factors is less than the number of variables or number of elements analyzed. The method involves interpreting the structure within a variance-covariance matrix of a multivariate data set and assigning the various elements of the matrix to groups (factors) on the basis of a common variability of these elements. A factor is a vector that is weighted proportionally to the amount of the total variance that it represents.

There are two methods of factor analysis, R-mode and Q-mode. Q-mode factor analysis investigates the interrelationships between individual samples, whereas R-mode factor analysis investigates the interrelationships in a matrix of correlations between variables. R-mode factor analysis can be used to identify groups of elements (variables) that have common associations, for example, a group of elements that represents a certain rock type (a lithologic factor), or a group that represents a type of- or model for-mineralization (a mineralizing factor).

R-mode factor analysis (Koch and Link, 1971) was used on the Puerto Rico geochemical stream sediment data to identify associations as geochemically related groups of elements.

These groups or "factors" were based on the correlation coefficients of the elements (table 4; table 5). Individual factors show predominant lithologies and mineral associations.

Factor analysis cannot be performed on data that contains nonnumeric or qualified values. The geochemical data sets for Puerto Rico, appendix D, contain many analyses that are qualified. Qualified values are indicated as follows: "N," not detected at the lower limit of analytical determination, "L," detected, but below the lower limit of determination, or "G," detected at greater than the upper limit of determination. In order to resolve problems with qualified data, a computer program was run on each data set to replace the qualified data with numeric data. The qualified data were replaced as follows:

N: All values of an element qualified with a "N" were replaced with 0.3 times the lower limit of determination for that element.

L: All values of an element qualified with a "L" were replaced with 0.7 times the lower limit of determination for that element.

G: All values of an element qualified with a "G" were replaced with 1.5 times the upper limit of determination for that element.

For semiquantitative spectrographic data these replacement values correspond to approximately three reporting steps lower than the lower limit of determination for "N"' values, One step below the lower limit of determination for "L"' values, and one step above the upper limit of determination for "G" values.

Factor analyses - A number of R-mode factor analyses using varimax factor rotation were run on the combined "old" and "new" data sets. One series of R-mode factor analyses included the censored data, and another series had the censored data removed. Individual factor analyses were run using from 7 to 12 factors. The factor analyses generated from data sets that excluded censored data gave somewhat similar results to the factor analyses generated from data sets that included censored data, the difference being that when the highly censored data were included, the elements Ag, As, Bi, Cd, Mo, and Sb, in general, were added to the factors related to mineralization. The individual factor analyses selected for interpretation were based on the ability to explain the individual factors in geologic terms and on the total percent of variance within the data set that was resolved. For the Puerto Rican data sets, 9- 12 factors were geologically significant and explained approximately 70 percent of the variance (Marsh, 1993). Comparison of the factor analyses for the "old" and "new" data sets indicates that the individual factors are comparable and in many cases identical. Because of these similarities a new data set called "all" was generated by combining the "old" and "new" data sets. To make the "all" data set, many element analyses were deleted from the "new" data set, including most of the inductively coupled plasma-atomic emission spectrophotometry (ICP-AES) analyses (appendix D). Also, variations in analytical techniques were ignored because most of the samples (both "old" and "new") were analyzed by the standard semiquantitative spectrographic method. The resulting "all" data set showed analytical data for 23 elements in 2,785 samples. Basic statistics (table 6) and a table of correlation coefficients (Table 7) were generated for the "all" data set, similar to those for the "old" and "new" data sets.

A series of R-mode factor analyses were run on both the "all" data set containing the censored data and on the "all" data set from which the censored data were removed, using from 7 to 11 factors (Marsh, 1993). For interpretation of the "all" data set containing the censored data, a ten-factor model was chosen that accounted for 69 percent of the variance (table 8). For interpretation of the "all" data set from which the highly censored data were removed, a nine-factor model was chosen that accounted for 71 percent of the variance (table 9). In the following discussion of the individual factors the nine-factor model, which excludes the censored data, is used. The ten-factor model, which includes the censored data, is referred to where the additional elements aid in the interpretation (table 8). These two factor models are generally equivalent, but the individual factors do not necessarily correspond. Where differences occur, they are noted.

The R-mode factor analysis program also creates a data file that contains a factor "score" for each sample in the data set. A score is calculated for each factor of each sample, and a high positive score indicates that the factor is dominant in that sample. A high negative score indicates that the factor is not representative for that sample. For this interpretation a positive score of +1 and a negative score of -1 were considered to be anomalous. These scores were plotted on a map of geologic terranes and (or) the permissive mineral deposit terranes, depending on whether the factors were related to lithology or mineralization, respectively. These factor score-plots are shown in figures 23 - 35 and are discussed in the geochemical interpretation of the factors and in the interpretation of individual deposit types.

Discussion of factors - The following is a discussion of the individual factors generated from the R-mode factor analysis of the "all" geochemical data set.

Factor 1. -- This factor has high positive loadings for Fe, Ti, V, Y, and Zr which make up a suite of elements that characterizes igneous rocks. When the highly censored data are included there are no changes and this factor becomes factor 7 (table 8). The factor score plot (fig. 23) shows anomalous sample localities that define the major intrusive bodies on the island including the San Lorenzo and Utuado batholiths. A clustering of anomalous sample localities occurs in the northwestern part of the island, northeast of Mayaguez, probably represents a more dominant acid to intermediate intrusive component of the volcaniclastic rocks in this area.

Factor 2. - This factor has high positive loadings for magnesium, cobalt, chromium, and nickel, which make up a suite of elements that can represent both lithology and mineralization. Lithologies represented are mafic to ultramafic rocks and laterite and include ophiolite sequences. Podiform chromite, nickel laterite, and platinum-group elements all can occur in these rock types. When the highly censored data are included there are no changes and this factor remains factor 2 (table 8). The factor-score plot (fig. 24) shows a clustering of anomalous sample localities around the known areas of ultramafic rocks in the southwestern part of the island. Another area of anomalous sample localities in the north-central part of the island, in the volcaniclastic terrane, corresponds, approximately, to the areas of anomalous sample localities shown for factors 3 and 6. These three factors combined would be consistent with a mafic rock terrane, but none is known to exist. Analytical values for samples from this area, although anomalous, are significantly lower than those for samples from the ultramafic rocks in the southwestern part of the island (appendix D) and may indicate the presence of basalt that contains mafic minerals such as chromian diopside, which would account for elevated values of magnesium and chromium.

Factor 3. - This factor has high positive loadings for calcium and strontium and a high negative loading for zinc. These elements are characteristic of a lithologic factor, mainly limestone and calcium bearing sedimentary rocks. When censored data are included (factor 5, table 8) the moderately positive factor loading for lead is added and the negative loading for zinc disappears. The factor-score plot (fig. 25) shows clusters of anomalous sample localities in the non volcaniclastic units that include the limestone terrane in the northern part of the island and the alluvial plains around the edge of the island. Some anomalous sample localities scattered throughout the rest of the island probably represent small limestone units in the volcaniclastic and basalt and chert terranes. A cluster of anomalous sample localities in and near the Utuado batholith (Intrusive and Structural Map), in the north-central part of the island, probably represent calcite veining, altered rock, and minor lead-zinc minerals because much of this terrane is mineralized. Another group of anomalous sample localities partially coincides with anomalous sample localities for factor 2 in the north-central part of the island and may represent either altered rock or calcite veining.

Factor 4. - This factor has high positive loadings for Ti, Mn, Sc, V, and Y, which make up a suite of elements characteristic of a lithologic factor, mainly mafic volcanic, volcaniclastic, and metavolcanic rocks and submarine basalt and chert. Factor 4 also has moderately positive factor loadings for iron, magnesium, and zinc, elements that are indicative of volcanic terrane. When the highly censored data are included, this factor becomes equivalent to factor 1 (table 8) and the moderately positive loading for barium is substituted for the moderately positive loading for zinc. The factor-score plot on the generalized geologic map (fig. 26) shows the preponderance of anomalous sample localities for factor 4 in the volcaniclastic rocks in the western third of the island, many clustered north of Mayaguez. The remainder is scattered throughout this rock type with an additional clustering of anomalous sample localities in the submarine basalt and chert west of the San Lorenzo batholith. The area of high negative loadings for factor 4 covering the entire area of the Utuado batholith in the west-central part of the island and part of the San Lorenzo batholith in the southeastern part of the island indicates that the chemical composition of these intrusive rocks is completely different from that of the surrounding volcaniclastic host rocks and, in the case of the Utuado Batholith, may be indicative of alteration and mineralization.

Factor 5. - This factor has high positive loadings for lead and zinc and a moderately positive loading for manganese. These elements are characteristic of base-metal mineralization as veins and possible elemental zoning around porphyry copper-molybdenum-gold deposits, of volcanogenic manganese deposits, and of Kuroko-type massive sulfide deposits (figs. 27 and 28). When the highly censored data are included, this factor becomes equivalent to factor 3 (table 8) and the factor loading for manganese becomes highly positive with a moderately positive factor loading for Fe added. The factor-score plot on a base map showing the igneous rocks and the porphyry copper terrane (fig. 29) show three clusters of anomalous sample localities: (1) around the known porphyry copper-gold deposits adjacent to the Utuado batholith in the west-central part of the island, (2) around the known porphyry-molybdenum occurrences in the northeastern part of the island, and (3) around the copper skarn occurrences in the east-central part of the island. Many of the anomalous sample localities in the western part of the island coincide with the margins of the volcanogenic manganese and Kuroko-type massive sulfide terrane (fig. 28). Other scattered anomalous sample localities in the volcaniclastic and basalt and chert terranes probably represent polymetallic vein occurrences.

Factor 6. - This factor has a high positive loading for barium, and, although no other loadings are listed, a moderately positive loading of .1933 for Magnesium is present, just below the cut off value of .2000. Factor 6 also has a moderately negative loading for zinc. When highly censored data are included, the barium-magnesium factor 6 (table 9) is no longer present and barium is associated with gold and lead (factor 6, table 8) and with tin (factor 10, table 8), both of these factors representing mineralization. The factor-score plot for the uncensored data shows several areas of anomalous sample localities, most of which are in the volcaniclastic terrane (fig. 30). Two exceptions to this relationship are the cluster of anomalous sample localities in granodiorite of the San Lorenzo batholith in the southeastern part of the island and the small cluster of anomalous sample localities around a small pluton in the north-central part of the island (fig. 31). These samples may represent a barium-rich phase of the plutons or may represent hydrothermal barite veins. The four other clusters of anomalous sample localities all occur in the volcaniclastic terrane (fig. 30). One cluster, in the northeastern part of the island, approximately corresponds to an area of anomalous sample localities shown for factors 2 and 3. These three factors combined would be consistent with a mafic rock terrane, but none is known to exist in this area. If, however, the actual anomalous values of these samples are examined (appendix D) they appear to mostly be of lesser magnitude than those found in the other anomalous areas. Mafic minerals in the volcaniclastic rocks in this part of the northeastern part of the island could be causing this area of anomalies. For example, chromium diopside in basalt would account for the higher than normal concentrations of chromium and magnesium in these rocks. Factor 6 anomalies also occur around the ultramafic terrane in the southwestern part of the island and in three areas in the central part of the island. These areas do not relate to any known mineral occurrences (Metallic Mineral Occurrences Map) and may be related to chloritic alteration and barite around a Kuroko-type massive sulfide or exhalative type deposit (Cox and Singer, 1986).

Factor 7. - This factor has high positive loadings for iron and copper and moderately positive loadings for magnesium, vanadium, and zinc. These elements represent porphyry copper-gold and porphyry copper mineralization. The factor score plot (fig. 32) shows most of the anomalous sample localities around the western part of the porphyry copper terrane, where there are known porphyry copper-gold deposits. An additional cluster of anomalous sample localities occurs near some small intrusive bodies in the north-central part of the island, and a small cluster of anomalous sample localities lies just northeast of Mayaguez, in the volcaniclastic terrane. When the highly censored data are included copper is present in two mineralization factors (factors 4 and 8, table 8) that represent porphyry copper deposits. In factor 4 has high positive loadings for copper and silver and represents mineralization. Factor 8 has a high positive loading for iron and molybdenum and the loading for copper becomes only moderately positive along with magnesium, lead, vanadium, and zinc.

Factor 8. - This factor is a single-element factor showing a high positive loading for boron. When the highly censored data are included boron is in factor 9 and the moderately positive loading for Pb is added (table 8). The factor-score plot (fig. 33) shows that most of the anomalous sample localities are lithologically related, in or adjacent to areas of the submarine basalt and chert terrane. Exceptions to this relationship are the cluster of anomalous sample localities at the north end of a pluton in the south-central part of the island and a cluster along the contact of the volcaniclastic terrane with the non-volcaniclastic terrane in the northwestern part of the island. Anomalies related to the pluton may represent mineralization or they may be related to alteration of the volcaniclastic rocks nearby. The anomalous sample localities in the northwestern part of the island appear to be lithologically related and may represent tourmaline bearing metavolcanic rocks or, where they coincide with anomalous sample localities for factor 9 (gold), may represent low-sulfide gold-quartz veins (Cox and Singer, 1984).

Factor 9. - This factor is also a single-element factor and shows a high positive loading for gold. In an eight factor model this factor (gold) is included in factor 6, the porphyry copper factor. Indeed, trace gold in soils has been used as an indicator element for the porphyry copper-gold deposits in the west-central part of the island (Learned and Boissen, 1973). When the highly censored data are included gold is in factor 6 (table 8). This factor also contains a high positive loading for barium and a moderately positive loading for lead. The factor-score plot (figure 34; figure 35) shows that the anomalous sample localities for the gold factor are related to the permissive mineral deposit terranes (map 1; map 2). Anomalous sample localities are clustered around the known porphyry copper-gold deposits in the west-central part of the island, related to placer deposits in the northeastern part of the island, and near the areas of epithermal quartz-alunite-gold. Anomalous sample localities are also clustered in the drainage basin of the Río Cibuco and may represent a placer potential downstream (fig. 34). The anomalous concentration of gold in this area is also reflected in 'Silt heavy-mineral distributions in the Rio Cibuco system and adjacent rivers of north-central Puerto Rico' by Poppe and others, contained within this publication.

Geochemical interpretation

Mineral resource terranes

The analytical results for the stream sediments reveal complex patterns of anomalously high values for many elements, and many of these anomalies can be attributed to various hydrothermal mineralization processes on the island. On the basis of these data and data from geophysics and geology, terranes permissive for mineral resources have been identified on the island of Puerto Rico (Permissive terrane map 1 and map 2). In addition, there is a possibility of a zircon placer terrane around the San Lorenzo batholith in the southeastern part of the island and of shoreline titanium placers around the island.

Geochemical maps

Cumulative frequency plots for elements (figs. 1 - 22) were used to determine the 90th percentile of the data. All values above the 90th percentile were plotted on the maps and ranges of values were used as noted.

Deposit models

The following discussion focuses on the geochemical data derived from stream-sediment samples and interpretation of anomaly patterns in relation to permissive terranes, known occurrences, and depositional terranes. The individual deposit models discussed below are described in detail in the Mineral Deposit Summary Sheet.

Podiform chromite and nickel laterite

Although no podiform chromite deposits are known to occur in Puerto Rico, an area of permissive terrane has been delineated. The geochemical suite of chromium, cobalt, and nickel (figure 24) characterizes this terrane, and most of the anomalous values for these elements are for samples from localities clustered around the mapped outcrops of mafic and ultramafic rocks in southwestern Puerto Rico; the factor plot for the Mg, Co, Cr, and Ni factor (fig. 24) closely corresponds to the geologic map of these rocks. There is another population of anomalies hosted mostly in marine Cretaceous volcaniclastic rocks in the north-central part of the island, in the Corozal and Naranjito quadrangles. There are 34 geologic units in the marine Cretaceous volcaniclastic terrane, but the anomalous area is confined mostly to the following map units; Kcam, Kcan, Keo, Kln, Kmag, Kman, Kpa, Krf, and Kv. The most common rock type in these formations is andesitic and basaltic lava followed by volcanic siltstone, sandstone, and breccia.

Crustal abundances for Co, Cr, and Ni are approximately 50, 170, and 140 parts per million (ppm) (table 3). Anomalies for these elements in this area are somewhat above these values and represent either unmapped more mafic lithologies, mafic minerals in the andesitic and basaltic lava, or possible mineralized rock. The map of nickel-cobalt anomalies show a broader distribution of cobalt throughout the marine Cretaceous volcaniclastic terrane and generally represents the lower range (50-150 ppm) of cobalt. This range is just slightly higher than crustal abundance and is considered within normal range for these rock types.

There are known nickel laterite deposits and located in the mafic and amphibolite terrane in southwestern Puerto Rico. The terrane favorable for this deposit type is the same as that favorable for podiform chromite and the related geochemical suite is similar. Although the Mg, Co, Cr, and Ni geochemical suite is present at anomalous sample localities the north-central part of the island, the volcaniclastic marine Cretaceous rocks are not conducive to the formation of nickel laterites.

Porphyry copper and porphyry copper-gold

These two deposit types are closely related, and the porphyry copper terrane is favorable for deposits fitting both these models. There are seven known deposits and ten occurrences of porphyry copper and porphyry copper-gold on the island. All but five occurrences fall inside this terrane. Copper anomalies are scattered throughout the porphyry copper terrane, and most are related to Cretaceous and Tertiary intrusive rocks, the most intense anomalies being in the area of porphyry copper-gold deposits in the west-central part of the island. This is also reflected in factor 7 of the R-mode factor analysis (table 9) and the factor-score plot for factor 7 (fig. 32). This area also has the most intense anomalies for gold and molybdenum, and minor anomalies for tin. Some of the known occurrences are not defined by anomalous concentrations of copper in stream-sediment samples, especially those occurrences outside the porphyry copper terrane. This may be due to low sampling density and the fact that all these occurrences may be rather small and poorly exposed. More detailed sampling in specific areas of known occurrences would probably give additional copper anomalies. There are two areas that contain anomalous concentrations for copper, gold, molybdenum, and tin that do not contain known mineral occurrences and may warrant further investigation. One is an area approximately 20 km east of the known porphyry copper-gold deposits. Anomalies in this area are centered on a cluster of small Tertiary plutons along the east margin of the Utuado batholith. This area also contains the localities of several anomalous samples on the factor score plot for factor 7 (fig. 32). A northwest-trending zone of copper-tin anomalies in the south-central part of the island contains a known porphyry copper deposit and three polymetallic vein occurrences, but it is mostly devoid of known mineral occurrences.

Copper and iron skarns

Terranes favorable for copper and iron skarn deposits were identified around the Río Blanco stock and San Lorenzo batholith. Of all the elements analyzed in the geochemical survey, only some scattered tin anomalies appear to be associated with the skarn terrane. There are scattered anomalies for copper, zinc, lead, and gold but no definite pattern or grouping of anomalies. Most of the known skarn occurrences are in marine Cretaceous volcaniclastic rocks to the north of the San Lorenzo batholith. There may be fewer anomalies in this terrane due to the lower sample density, because skarn deposits tend to be rather small and irregular. The preponderance of the tin anomalies are on the west side of the San Lorenzo batholith in Cretaceous and Tertiary extrusive rocks and may suggest unidentified skarn deposits or pegmatite. Scattered gold, copper, molybdenum anomalies and the only tungsten anomaly occur in drainage basins around the Río Blanco stock and may indicate a potential for tungsten-bearing skarn.

Polymetallic veins

By far the most numerous metallic mineral occurrences are polymetallic veins, 59 occurrences and 2 deposits being scattered throughout the island. Geochemical anomalies related to this deposit type are also scattered throughout the island and samples anomalous in factor 4, which is indicative of intermediate to acid igneous rocks, show a similar island-wide distribution. One area containing 16 of the known occurrences is also within the porphyry copper terrane, related to the known porphyry copper-gold deposits in the west-central part of the island. Copper, lead, zinc, and silver anomalies group in this area and probably represent polymetallic vein occurrences peripheral to the porphyry copper-gold deposits. Another grouping of nine occurrences in the south-central part of the island in marine Tertiary volcaniclastic rocks is not geochemically defined because of low sample density.

Volcanogenic manganese and Kuroko-type massive sulfide

These two deposit types are outlined by one terrane in volcaniclastic rocks in the west and west - central part of the island. The geochemical signature for volcanogenic manganese is Mn, Cu, Pb, Zn, and Ba and for Kuroko massive sulfide is Cu, Zn, Pb, Ba, As, Ag, Au, Se, Sn, Bi, and Fe. Co, Pb, Zn, Sn, Au, and Ag occur as scattered anomalies in this terrane, in which Cu and Zn anomalies predominant, especially in the western part. Anomalous sample localities for the factor-score plot of factor 5 (Pb, Zn, and Mn; fig. 28) are also common in this part of the terrane.

Epithermal quartz-alunite gold

Most of the known terranes for this model are represented by anomalies for Au, Ag, Cu, Pb, and Zn, but especially for Cu and Au. Since the geochemical signature for this model can include almost any combination of base and precious metals, depending on the level of the mineralized system exposed at the surface, it is very difficult to establish geochemical anomaly patterns for this model.

Placer gold and platinum-group elements

The factor score plot for factor 9 Au (fig. 34; fig.35) shows potential gold placer terranes and localities for samples containing gold. Some gold anomalies define drainage basins that are permissive for placer deposits in the northwestern and north-central part of the island. Some of these drainage basins contain areas of past production or contain known deposits and the mineralogy from one, Río Cibuco, has been studied in detail (see Poppe, and others, ‘Silt heavy-mineral distributions in the Rio Cibuco system…, this volume).

Shoreline placer titanium

Although the four known placer titanium occurrences are all along the north coast of the island, the bulk of the titanium anomalies in stream sediments occur in the volcaniclastic rocks in the western part of the island. The mineralogy of the titanium in these samples is unknown, but if sufficient ilmenite ($FeTiO_3$) is present there may be potential for placer deposits along the west shoreline. There are also a number of large titanium anomalies (1,000-2,000 PPM) surrounding the San Lorenzo batholith in the southeastern part of the island, and there is a shoreline titanium placer potential in this area. This area is also characterized by zirconium anomalies, indicating that the San Lorenzo batholith may be a more felsic intrusion than others on the island. If this is the case, then shoreline placers may also contain zircon and possibly other rare-earth minerals.

Copper Manto

The area of copper Manto terrane is in the north-central part of the island, is confined to the Pozas Formation, and is relatively small. Although there are three known occurrences near the northeast border of this terrane, there is little geochemical evidence for this model except for a few copper anomalies in the central part and a few anomalous sample localities for factor 7 on the factor score plot for copper (fig. 32).

Summary

The geochemical data for the stream-sediment samples from Puerto Rico generally supports and helps define the mineral deposit models and permissive terranes on the island as well as identifying possible additional areas of presently unknown mineralization. The geochemistry and factor analysis also help differentiate lithology from mineralization.

GEOCHEMISTRY OF ISLA DE VIEQUES AND ISLA DE CULEBRA

Isla de Vieques

Introduction -- Isla de Vieques was geochemically sampled in 1972, and Learned and others (1973) published a report describing the results. A soil-sample survey of the island was conducted, rather than a stream-sediment survey, because drainage basins are poorly developed and commonly filled with colluvium and, where near populated areas, highly contaminated. A total of 421 soil samples were taken of the "C" horizon (weathered bedrock) at 0.5-km intervals on northwest-trending traverses spaced approximately 1 km apart. The soil samples were analyzed for 30 elements by semiquantitative emission spectroscopy (Grimes and Marranzino, 1968). Gold and zinc were also determined by atomic-absorption methods (Ward and others, 1969 and Thompson and others, 1968). All geochemical data from the regional soil geochemical survey are published in USGS Open-File Reports 73-1866, 92-353-A and 92-353-B (Learned and others, 1973 and Marsh, 1992) and are included in appendix D, this report.

Geology -- The geology of the island is dominated by Late Cretaceous intrusions (quartz-diorite, diorite, and granodiorite) that have intruded a thick (greater than 700 m) section of Upper Cretaceous andesite, tuff, breccia, and limestone (G.R. Grove, unpub. data, 1972). These rocks all exhibit some degree of propylitization and have been contact metamorphosed to hornblende-hornfels facies near the contact with the intrusions. A zone of intense hydrothermal alteration extends along the northeast coast from just east of Santa Maria to 2 km east of Punta Goleta. This area is characterized by severe bleaching and oxidation and by numerous quartz veins. The quartz veins range in size from 1 to 2 mm to more than 0.5 m and contain magnetite, pyrite, chalcopyrite, and molybdenite. Late, fine-grained diorite dikes intrude both the plutonic and volcanic rocks.

Statistical methods -- The soil geochemical data for Isla de Vieques were examined and univariate statistics were generated (table 10). From the univariate statistics, cumulative frequency plots were generated for 11 elements (figs. 36 - 46). For the purposes of this study geochemical values in the 90th percentile or above were considered to be anomalous. Where feasible, arbitrary ranges of values were used in the element plots. In the case of highly censored data, as for gold, any reported value was generally at or above the 90th percentile and was used in the element plot.

Correlation - In addition to the above statistics, a table of correlation coefficients was generated (table 11). This table shows three different things; (1) correlations between elements, (2) the standard deviation for each element, and (3) the number of samples involved in making the correlation. Correlations are shown in the upper half of the tables. Those in **bold** and **bold shaded** typeface are statistically significant and correlate at the 99 percent confidence level (99 percent of the time the correlation is significant and not the result of a random event) for the elements shown. The correlations indicate lithogeochemical associations as well as associations related to mineralization. The number of samples involved in each correlation is shown in the lower half of the tables. The standard deviations for each element are shown in the middle of the tables. To read the tables, find the element of interest (either vertically or horizontally), move across or down to the other element of interest and note the number. If you are in the upper half of the table the number will be the correlation coefficient and if you are in the lower half of the table the number will be the number of samples involved in the correlation calculation. If you look at the same element along both the vertical and horizontal axes, the resulting number will be the standard deviation for that element (shown in UNDERLINE typeface).

R-mode factor analysis -- In order to help sort the lithogeochemical associations from those related to possible mineralization, an R-mode factor analysis was run initially on the entire soil geochemical data set, including highly censored elements (elements for which there were less than 38% valid determinations) (table 12). As with the stream-sediment geochemical data for

Puerto Rico, qualified data were replaced with numeric data (see previous discussion of multivariate analyses). A second factor analysis was run on a modified data set from which the highly censored elements removed (table 13). A six-factor model was selected for both the entire soil geochemical data set and for the data set with the highly censored data removed that accounted for 61 percent and 73 percent of the total variance in the data, respectively. Factor loadings for each element, both positive and negative, are shown in table 11 and table 12. Both factor models gave somewhat similar results, the difference being that with the entire data set the censored elements Ag, Au, Bi, and Mo were added to the factors related to mineralization.

Factor 1. -- In both factor analyses, factor 1 has high positive loadings for Fe, Mg, Ti, Mn, Co, Sc, V, and Y which make up a suite of elements characteristic of a lithologic factor. With the entire data set factor 1 also has high positive factor loadings fro chromium and nickel and a moderate positive loading for copper. When highly censored data are removed (table 13) factor 1 has a high positive loading for copper and a moderately positive loading for chromium and nickel. Factor 1 can be interpreted to represent ferromagnesian-bearing rocks, which would include the igneous intrusive, volcanic, and volcaniclastic rocks of the island.

Factor 2. -- When all the data are included, factor 2 has moderately positive loadings for B, Co, Mo, Sc, Y, and Zn, and high negative loadings for Mn, Ba, and Sr (table 12). Factor 2 can be interpreted to represent the diorite-granodiorite pluton that is mineralized in some areas. The high negative loadings for barium and strontium indicate that the large barium anomaly in the southwestern part of the island probably is not related to the mafic chemistry of the pluton and indicates an alteration phenomenon. With the highly censored data removed, factor 2 is simpler, having high positive loadings for manganese, barium, and strontium (table 13). This geochemical suite could indicate either a given rock type and (or) alteration. Barium and strontium are commonly associated with limestone, and although uncommon, there is a small area of limestone at the eastern end of the island. Significantly, however, all the anomalous barium values are for samples in the southwestern part of the island, mostly in the diorite-granodiorite intrusive rocks. This is interpreted to represent a secondary alteration phenomenon.

Factor 3 -- Factor 3 for the entire soil data set (table 12) is equivalent to factor 4 in the modified data set from which the highly censored elements have been removed (table 13). Factor 3 for the entire data set is a mineralization factor and has high positive loadings for Pb and Zn and moderately positive loadings for Au, Ag, and Mn (table 12). The suite of elements in factor 3 can be interpreted to represent base- and precious-metal deposit types related to the intrusive rocks on the island. Factor 3 for the modified data set has high positive loadings for yttrium and zirconium, moderately positive loadings for manganese, and a high negative loading for calcium; it can be interpreted to represent a given rock type and (or) alteration (table 13). These elements probably represent a geochemical contribution from the diorite-granodiorite pluton, and the high negative factor for calcium probably indicates a more sodic feldspar composition.

Factor 4. -- Factor 4 for the entire soil data set is equivalent to factor 3 in the modified data set, from which the highly censored elements have been removed. Factor 4 for the entire data set is a lithologic and (or) alteration factor having high positive loadings for Mn, Ba, Y and Zr, moderately positive loading for Ti, and high negative loadings for Ca, Cr, and Ni (table 12). This is interpreted to represent the diorite-granodiorite intrusive rocks and alteration at the contact with the volcanic and volcaniclastic rocks. The high negative loadings indicate that the mafic volcanic rocks are not contributing to this factor. Factor 4 for the modified data set has high positive loadings for lead and zinc and a moderately positive loading for manganese and is interpreted to represent base- and precious-metal mineralization (table 13). With the censored data removed, especially gold and silver, the suite of elements representing base- and precious-metals is somewhat simplified but still significant.

Factor 5. -- For the entire data set (table 12), factor 5 is interpreted to represent a given rock type; it has high positive loadings for beryllium and lanthanum and moderately positive loadings for boron and zirconium. This factor probably represents the diorite-granodiorite intrusive rocks. For the modified data set factor 5 (table 13) is interpreted to also represent a given rock type; it has high positive loadings for Cr and Ni and moderate positive loadings for Co, Sc, and Zn. This elemental suite probably represents the mafic volcanic (hornblende andesite) and volcaniclastic rocks of the island that are intruded by the diorite-granodiorite pluton.

Factor 6. -- Factor 6 for the entire data (table 12) set is another mineralization factor having high positive loadings for Ag, Cu, and Mo, and moderate positive loadings for Bi, Pb, and Au. This suite of elements is interpreted to represent a porphyry copper deposit type, model 17 from Cox and Singer (1986). Factor 6 for the modified data (table 13) is another lithologic factor having a high positive loading for boron, moderately positive loadings for calcium and yttrium, and a high negative loading for copper. This factor is interpreted to represent the non-altered and non-mineralized diorite-granodiorite igneous rocks.

Geochemical interpretation -- Results from the geochemical soil sampling indicate three areas on Isla de Vieques that are of potential economic interest: area 1: the east end of the zone of intensive alteration in Cretaceous volcanic rocks along the northeast coast; area 2: a central zone of propylitized rocks trending northwest in the center of the island along the contact between plutonic and volcanic rocks; and area 3: an area in the northwestern part of the island spatially related to the contact of the western pluton and Upper Cretaceous andesite and tuff units. Cerro El Buey, immediately south of this area, is a coarse-grained hornblende gabbro that intrudes the western pluton. Gravity data suggest that Cerro El Buey may be the southern tip of a much larger feature. Cerro El Buey may be contributing to the geochemical anomalies in this area. All three areas are anomalous in iron (greater than 7 percent) and titanium (greater than 0.7 percent)

Area 1. -- Area 1 is the east end of the zone of intense hydrothermal alteration along the northeast coast. Analysis of geochemical soil samples indicated anomalies in Fe, Ti, Cu, Zn, Mo, Sn, Ag, and Au. This geochemical suite of elements is indicative of copper skarn mineralization related to a porphyry copper system (model 18b, Cox and Singer, 1986). The anomalous concentrations of iron and titanium in the area, along with anomalous concentrations of magnesium are probably the result of the intense hydrothermal alteration of the Upper Cretaceous volcanic rocks (andesite, tuff, and breccia). The geochemical anomalies combined with the geologic observations of the intense hydrothermal alteration and iron- and manganese-stained boxwork quartz veins containing chalcopyrite and pyrite make area 1 the most significant zone of mineralization on the island.

Area 2. -- Area 2 is along the eastern contact of the western quartz-diorite pluton with Upper Cretaceous metavolcanic rocks south of Isabele Segunda and east of Destino (G.R. Grove, unpub. data, 1972). Here, copper occurs as chalcopyrite in quartz veins in the quartz-diorite pluton. Geochemical soil samples show anomalies in copper, gold, and molybdenum indicative again of copper-skarn mineralization. Anomalies of iron, titanium, and magnesium are probably the result of contact metamorphism and hydrothermal alteration. Area 2 contains anomalies of fewer elements in the geochemical suite related to copper skarns, is smaller in areal extent, and apparently has less potential for copper skarn deposits than does Area 1.

Area 3. -- Area 3 is at the west end of the western pluton and is along its contact with Upper Cretaceous metavolcanic rocks. This area contains anomalous amounts of iron, titanium, copper, and gold. As with the other two areas, area 3 shows some evidence of hydrothermal alteration and copper-skarn mineralization. Area 3 also is just north of Cerro El Buey, an area of copper anomalies.

Additional single-point anomalies in the geochemical suite related to copper-skarn - copper-porphyry mineralization are scattered throughout the area of Late Cretaceous diorite and probably reflect small mineralized siliceous zones and veins. Lithogeochemical anomalies of chromium, nickel, and cobalt occur throughout the areas of volcanic and metavolcanic rocks on the island and represent the mafic nature of these units. An area of intense barium anomalies (see appendix D) occurs at the southwestern end of the island and is partially coincident with a small grouping of manganese anomalies. The area is mapped as part of the western diorite pluton (G.R. Grove, unpub. data, 1972), and there are no reported occurrences of barite or barite veins. These anomalies are probably due to alteration.

Isla de Culebra

Introduction -- The small island of Culebra was geochemically sampled in late 1970 as part of a study to determine the island's natural resources, development potential, and socio-economic aspects (Commonwealth of Puerto Rico, 1970). Because of the lack of active streams on the island, geochemical samples of dry streambed material were collected. This material included pebbles and cobbles showing the most intense iron staining and any material showing traces of mineralization. A total of 41 samples were collected and analyzed for 30 elements by emission spectrography (Grimes and Maranzino, 1968). Gold was also determined by an atomic-absorption method (Ward and others, 1969).

Geology -- Most of the island is composed of andesite lava of probable Cretaceous age showing pillow structures. These are overlain by andesite tuff along the northeast coast. The tuff and lava have been intruded by diorite in the north-central part of the island.

Geochemistry -- Of the 41 samples analyzed, only nine contained anomalous concentrations of any elements commonly associated with mineralization and these were only weakly anomalous for one element, copper (100-150 PPM) (see appendix D). Since this is only slightly above crustal abundance (table 3) and since the semiquantitative spectrographic method was used for analysis, these numbers are probably within normal range for these rocks. None of the samples contained any other elements of interest above crustal abundance. Since no anomalous samples were identified from the geochemical data and because of the small number of samples, no statistics were run on the geochemical data from Isla de Culebra. There are no identified deposit types on the island, and no mineral deposit terranes were established. All geochemical data from the regional stream-sediment geochemical survey are published as Open-File Reports 92-353-A and 92-353-B (Marsh, 1992) and are included in appendix D, this report.