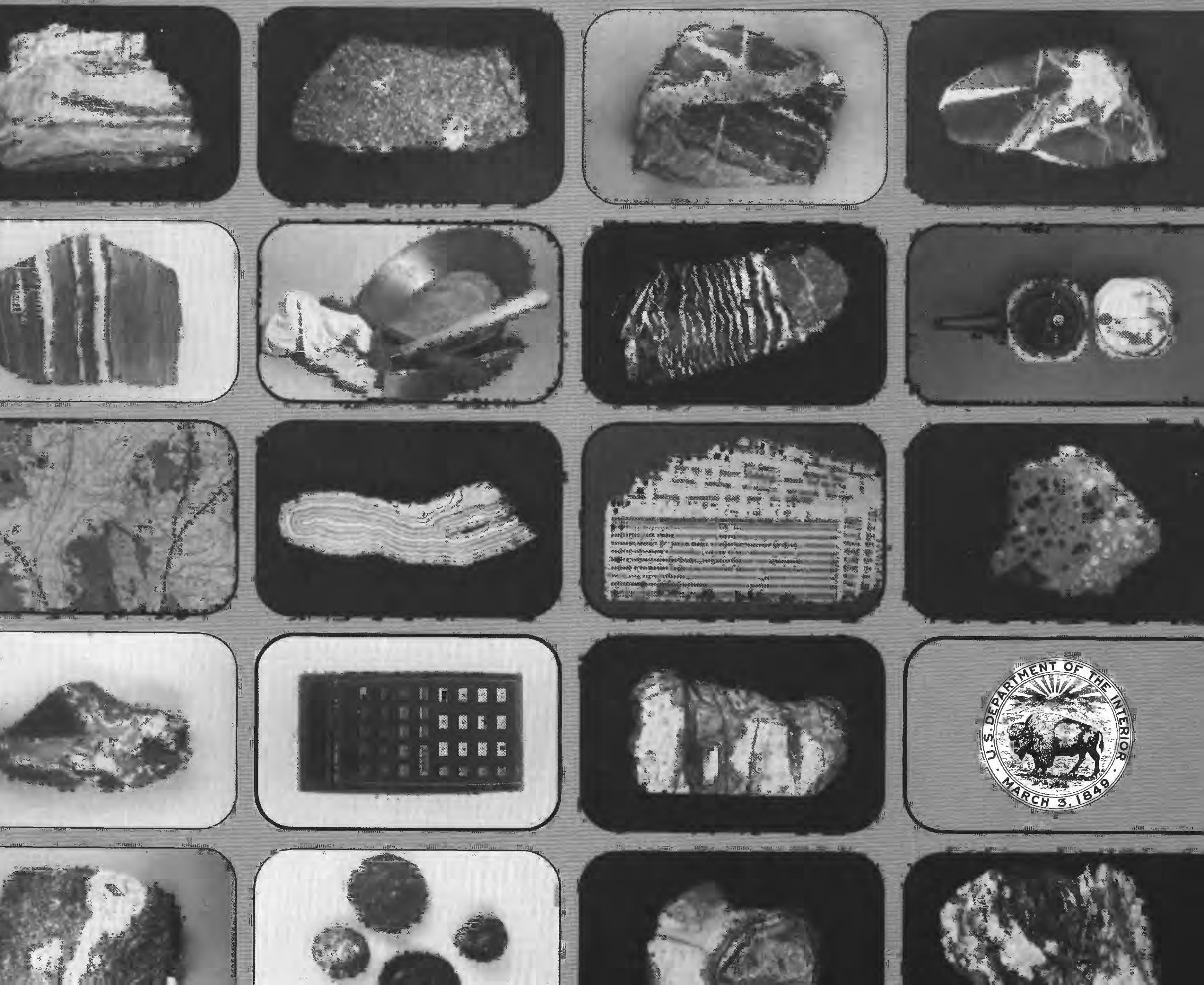
Grade and Tonnage Relationships Among Copper Deposits *and* Geochemical Exploration Techniques Applicable in the Search for Copper Deposits

GEOLOGICAL SURVEY PROFESSIONAL PAPER 907-A, B



COVER PHOTOGRAPHS

1	2	3	4
5		6	
	7		8
9		10	
11	12	13	14

1. Asbestos ore
2. Lead ore-Balmat Mine, N. Y.
3. Chromite-chromium ore, Wash.
4. Zinc ore-Friedensville, Pa.
5. Banded iron formation, Palmer, Michigan
6. Ribbon asbestos ore, Quebec, Canada
7. Manganese ore, banded rhodochrosite
8. Aluminum ore, bauxite, Georgia
9. Native copper ore, Keweenawan Peninsula, Mich.
10. Porphyry molybdenum ore, Colo.
11. Zinc ore, Edwards, N. Y.
12. Manganese nodules, ocean floor
13. Botryoidal fluorite ore, Poncha Springs, Colo.
14. Tungsten ore, North Carolina

Grade and Tonnage Relationships Among Copper Deposits

By D. A. SINGER, DENNIS P. COX, *and* LAWRENCE J. DREW

and

Geochemical Exploration Techniques Applicable in the Search for Copper Deposits

By MAURICE A. CHAFFEE

GEOLOGY AND RESOURCES OF COPPER DEPOSITS

GEOLOGICAL SURVEY PROFESSIONAL PAPER 907-A,B

U.S. DEPARTMENT OF THE INTERIOR
MARCH 3, 1849

UNITED STATES GOVERNMENT PRINTING OFFICE, WASHINGTON : 1975

UNITED STATES DEPARTMENT OF THE INTERIOR

THOMAS S. KLEPPE, *Secretary*

GEOLOGICAL SURVEY

V. E. McKelvey, ***Director***

First printing 1975
Second printing 1976

Library of Congress Cataloging in Publication Data

Singer, D. A.

Grade and tonnage relationships among copper deposits.

(Geology and resources of copper deposits)

(Geological Survey professional paper ; 907–A, 907–B)

Includes bibliographies.

Supt. of Docs. no.: 19.16:907–A.

1. Copper ores—United States. 2. Copper—Analysis. 3. Geochemical prospecting. I. Chaffee, Maurice A. Geochemical exploration techniques applicable in the search for copper deposits. 1975. II. Title. III. Series. IV. Series: United States. Geological Survey. Professional paper; 907–A, 907–B.

TN443.A5S54 553'.43'0973 74-23594

For sale by the Superintendent of Documents, U.S. Government Printing Office
Washington, D.C. 20402
Stock Number 024-001-02669-4

APPRAISAL OF MINERAL RESOURCES

Continuing appraisal of the mineral resources of the United States is conducted by the U.S. Geological Survey in accordance with the provisions of the Mining and Minerals Policy Act of 1970 (Public Law 91–631, Dec. 31, 1970). Total resources for purposes of these appraisal estimates includes currently minable resources (*reserves*) as well as those resources not yet discovered or not presently profitable to mine.

The mining of mineral deposits, once discovered, depends on geologic, economic, and technologic factors; however, identification of many deposits yet to be discovered, owing to incomplete knowledge of their distribution in the earth's crust, depends greatly on geologic availability and man's ingenuity. Consequently, appraisal of mineral resources results in approximations, subject to constant change as known deposits are depleted, new deposits are found, new extractive technology and uses are developed, and new geologic knowledge and theories indicate new areas favorable for exploration.

This professional paper discusses aspects of the geology of copper as a framework for appraising resources of this commodity in the light of today's technology, economics, and geologic knowledge.

Other Geological Survey publications relating to the appraisal of resources of specific mineral commodities include the following:

Professional Paper 820—"United States Mineral Resources"

Professional Paper 926—"Geology and Resources of Vanadium"

Professional Paper 933—"Geology and Resources of Fluorine"

Grade and Tonnage Relationships Among Copper Deposits

By D. A. SINGER, DENNIS P. COX, *and* LAWRENCE J. DREW

GEOLOGY AND RESOURCES OF COPPER DEPOSITS

GEOLOGICAL SURVEY PROFESSIONAL PAPER 907-A

An analysis of the relationships between grades and
tonnages of three types of copper deposits—
porphyry, massive sulfide, and strata-bound

U.S. DEPARTMENT OF THE INTERIOR
MARCH 3, 1849

UNITED STATES GOVERNMENT PRINTING OFFICE, WASHINGTON : 1975

CONTENTS

ILLUSTRATIONS

TABLES

GEOLOGY AND RESOURCES OF COPPER DEPOSITS

GRADE AND TONNAGE RELATIONSHIPS AMONG COPPER DEPOSITS

By D. A. SINGER, DENNIS P. COX, and LAWRENCE J. DREW

ABSTRACT

Three types of copper deposits—porphyry, strata-bound, and massive sulfide—are described, and the distributions of tonnages and grades for 267 deposits are compared with normal and lognormal frequency distributions. The relationships between grades and tonnages are analyzed by examining the correlation coefficients of these variables. Conclusions reached include the following: (1) Geologic factors influencing tonnage of a particular deposit type are probably distinct from those influencing grade; (2) frequency distributions of tonnages and grades approximate lognormality, making it possible to predict probability of various tonnage-grade classes and to test correlation between variables; (3) no significant correlation was found between tonnage and grade for porphyry or strata-bound deposits; (4) significant negative correlation between tonnage and grade was found for the massive sulfide subset, probably reflecting a mixture of high-grade low-tonnage massive ores, low-grade high-tonnage stockwork, and disseminated ores characteristic of some massive sulfide deposits; (5) significant negative correlation was found between tonnage and grade for the mixture of deposit types in the whole sample.

Extrapolation on the basis of the negative grade-tonnage correlation shown for the mixed population seems to imply the occurrence of large-tonnage very low grade deposits, which could be important in supplying future copper needs. This extrapolation is misleading, however, for both statistical and geological reasons. Furthermore, large-tonnage very low grade deposits in the porphyry class of the population are found to be very rare occurrences.

INTRODUCTION

It has become imperative to have reliable estimates of the resource potential of various areas and commodities so that alternatives may be considered in order to maintain an orderly supply of minerals. Estimates of the resource potential of an area or commodity must include both the unpublished ultimate reserves of known deposits and the undiscovered deposits that might be mined if found. In both cases it is useful to have estimates of the probabilities with which different grades and tonnages occur. This is often best accomplished by means of statistical models of the grades, tonnages, and the grade-tonnage relationships of the different types of occurrences of the commodity of interest. An analysis within each type of occurrence is necessary because the types may occur in diverse geologic environments and may be characterized by distinct statistical models.

In this study, the grades and tonnages of three types of copper deposits are compared with theoretical statistical models in order to build models of future discoveries. The grades of copper only are considered because of the difficulty of equating the different metals found in copper deposits. The three types—porphyry, strata-bound, and massive sulfide deposits—represent the world's main sources of copper at present. The observed frequency distributions of grades and tonnages are compared with the normal and lognormal frequency distributions. The relationships among grades and tonnages of the three deposit types are analyzed by examining the correlation coefficients of these variables. These relationships are useful both in building models of future discoveries and in testing the frequently implied inverse relationship between grade and tonnage. This relationship is often a hidden assumption in large highly aggregated mineral resource models, implying that improvements in technology can enlarge the supply of minerals.

ACKNOWLEDGMENTS

This study was greatly helped by discussions with and data supplied by G. H. Goudarzi of the U.S. Geological Survey and various industry geologists.

PORPHYRY COPPER DEPOSITS

Disseminated copper deposits, genetically related to felsic or intermediate intrusive igneous rocks, are called porphyry copper deposits. Copper minerals may occur as fine disseminated grains, in small crosscutting veinlets, or in thin coatings on joint surfaces. In most deposits, the copper ore body is mainly within the associated intrusive rock; but in some deposits, the surrounding rocks, particularly limestone, may be replaced by copper minerals. Copper minerals may also be deposited in breccia pipes or breccia veins, or in parallel or branching quartz veins sufficiently closely spaced to be extracted by mass-mining methods. All these ore types are believed to be closely related genetically and are commonly included in the porphyry copper classification.

Molybdenum, gold, and silver may be important byproducts, and lead, zinc, silver, and manganese deposits may be peripheral to the porphyry deposit. Replacement and vein deposits are usually found in a distinct zonal arrangement in the rocks surrounding a porphyry. Copper, in replacement ore bodies, may be within a few hundred metres of the intrusive lead-zinc silver deposits farther out, and manganèse or gold-silver deposits may be on the outer fringes.

Porphyry copper deposits generally have a complex history involving several stages of igneous intrusion, mineral deposition, and hydrothermal alteration. In some deposits such as San Manuel, Ariz. (Lowell and Guilbert, 1970), the late magmatic and deuteric stages are well represented. In others such as Butte, Mont. (Meyer, Shea, and Goddard, 1968), hydrothermal activity that postdates cooling of the intrusive body predominates. In still others such as Morenci, Ariz. (Moolick and Durek, 1966), oxidation and enrichment by descending surface waters have obliterated most of the minerals that may have been deposited in earlier stages. In most deposits, evidence for all three stages is found.

Factors influencing tonnage.—In deposits where mineralization is confined to an intrusive body, the tonnage of the deposit may be controlled mainly by the volume of the intrusion. Very few intrusions associated with porphyry copper mineralization are of batholithic proportions; in those that are, only a small part of the intrusion is mineralized or hydrothermally altered. In other deposits in which favorable wallrocks are mineralized, the size of the deposit may be dependent on the stratigraphic thickness of the favorable beds and on the width of the copper-rich mineral zones surrounding the porphyry deposit. This width is presumably dependent on the temperature, pressure, and hydrothermal conditions near the intrusion and on the physical character of adjacent host rocks.

Finally, in some deposits, postmineral faulting followed by erosion has had an obvious effect on the tonnage of ore. Ore bodies may be cut by major faults, and a large part may have been uplifted and destroyed by erosion.

Factors influencing grade.—Conditions favoring oxidation and enrichment of porphyry deposits have an important influence on grade. The factors include climatic and ground-water conditions from the time of the original uplift and erosion of the deposit to that of the present erosion cycle. The degree of fracturing of the rock is important as well as an abundance of pyrite that oxidizes readily to provide acid ground water.

Protore grades of porphyry deposits (the copper content before enrichment by descending waters) seldom exceed 1 percent. An important factor influencing protore grade may be the availability of sites favorable for deposition of copper minerals. Such sites include (1) carbonate wallrocks and (2) dispersed iron oxide and iron-magnesium silicate minerals in both wallrocks and intrusive bodies. A close spacing of fractures also influences protore grade, presumably by providing access for copper-bearing solutions to the available sites of deposition.

STRATA-BOUND AND STRATIFORM DEPOSITS IN SEDIMENTARY AND METAMORPHIC ROCKS

Strata-bound ore bodies locally cut across bedding but are confined to a single sequence of strata over large areas. Stratiform copper deposits have the form of a bed, concordant with strata of surrounding rocks, and are laterally continuous for a great distance relative to their thickness. Copper minerals commonly are disseminated in both these ore bodies, but, rarely, in some very high-grade deposits they form massive beds. Lead and zinc ore bodies may be zonally arranged outward from the copper-rich beds or may form separate beds in the same stratigraphic sequence. Cobalt, silver, and minor amounts of nickel and bismuth are found in some deposits; uranium, vanadium, and thorium are associated with copper in other types.

Origin of strata-bound deposits is the subject of great controversy. Some of the largest deposits are metamorphosed and show the effects of mobilization of copper and its redeposition in crosscutting fractures and noses of folds. Processes including direct sedimentary deposition, early stage diagenesis, ground-water mineralization, and hydrothermal ore deposition have been suggested to explain the origin of some deposits. Sulfur-reducing bacteria may have an important role in the precipitation of metal sulfides in sediments and sedimentary rocks. Metal-rich sediments underlying the hot brine pools in the Red Sea may be modern analogs of stratiform copper deposits, but the origin of these is also a matter of controversy.

Factors influencing tonnage.—A thick and laterally extensive ore-bearing stratum is probably the result of many processes, beginning with sedimentation and ending with remobilization of copper during diagenesis or metamorphism. As in porphyry deposits, faulting and folding can cause uplift and destruction of large parts of a mineralized bed.

Factors influencing grade—Original permeability of the sediment and abundance of organic matter, pyrite, or other possible copper-precipitating agents in the sediment are two factors that may influence grade. Abundance and activity of organisms may also be important, as well as many other factors now unknown. Downdip migration of copper during weathering may produce very high grade deposits by secondary enrichment.

MASSIVE SULFIDE DEPOSITS

Concordant lens-shaped deposits of copper-bearing massive pyrite are found in volcanic and sedimentary rocks. These deposits are generally more limited in areal extent than strata-bound disseminated deposits. Zinc, lead, and precious metals are found in massive sulfide ore bodies and may exceed copper in total value. Deposits may have discrete boundaries, passing from massive sulfide into barren wallrocks within a few centimetres. Low-grade ore bodies in stockworks of closely spaced quartz-chalcopyrite-pyrite veinlets are associated with some massive sulfide deposits, as are sedimentary beds of low-grade ore containing disseminated mineral fragments. Bedded deposits of manganese oxide, barite, or gypsum, and vein deposits of gold and silver may be closely associated in time and space with massive sulfide deposits.

Massive sulfide deposits are found in the eugeosynclinal or volcanogene parts of fold belts and in volcanic belts in Archean shield areas. Most deposits are strongly deformed by folds and faults clearly postdating the mineralization, and their origin is thus obscured. Some younger deposits, particularly the Kuroko deposits in the Miocene of Japan, show evidence of deposition on the sea floor by metal-rich exhalations from submarine volcanic eruptions (see, for example, Tatsumi and Watanabe, 1971). In these deposits, the low-grade ores in stockworks are believed to represent feeder channels in the underlying rock through which the exhalations passed, and the disseminated ores in sedimentary beds are believed to have been formed by the deposition of fine sulfide fragments scattered on the sea floor by the eruption activity.

Factors influencing tonnage.—Massive sulfide deposits vary greatly in physical size and tonnage. In those deposits whose origin is clear, the strength and duration of submarine fumarolic activity was the most important factor in determining tonnage. If a massive sulfide ore body is closely associated with stockwork or disseminated mineralization of economic grade, then the tonnage of the combined ore bodies may be large.

Factors influencing grade.—Grade is presumably controlled primarily by the copper content of the exhaled vapors and solutions relative to iron, zinc, and other metals. Copper content of these exhalates may be related to the type of associated volcanic rock. Anderson (1969) and others have shown that copper-bearing massive sulfide deposits are more commonly associated with mafic volcanic rocks and that lead-zinc varieties are associated with felsic volcanic rocks. The inclusion of large-tonnage disseminated and stockwork ores in a reserve estimate will greatly lower the average grade of the combined deposits. Secondary replacement of chalcopyrite and pyrite by chalcocite during weathering and enrichment is important in forming high-grade deposits under certain climatic and topographic conditions.

GEOLOGICAL CONSIDERATIONS OF TONNAGE AND GRADE RELATIONSHIPS

From the foregoing description of copper-deposit types, it becomes clear that these deposits are geologic entities having definite geologic boundaries. These boundaries represent the outer limits of the effects of unusual geologic processes that produce mineral deposits. Beyond these boundaries, "usual" varieties of rocks are found with copper content in the 5 to 150 parts per million (ppm) range. Copper deposits are not, therefore, merely high points or anomalies in a smoothly fluctuating curve of copper abundance in rocks.

The position of the deposit boundaries, and hence the tonnage of the deposit, is a function of the magnitude of the geologic systems involved, whether plutonic, volcanic, or sedimentary. To use a thermodynamic analogy, tonnage is an extensive variable. The abundance of copper minerals within these boundaries, that is, the grade, depends on a combination of factors relating to the intensity of the mineralization process, the concentration of the mineralizing solutions, the rate of change of those concentrations in the depositional process, and the availability of sites of deposition. Most importantly, grade is affected by repeated mineralization processes superimposed on each other (secondary enrichment). In thermodynamic parlance, grade is an intensive variable. Thus, it can be concluded that, in general, the grade of a deposit and the tonnage of a deposit are controlled by separate and distinct geologic factors.

NATURE OF DATA

The data used include the historical production plus the estimated reserves of each of 267 deposits. Copper grades used are weighted in the appropriate amount by the production and reserves. Rather than use data from the operations of a single mining unit, each deposit is considered as a geologic unit. For example, Miami, Inspiration, and Miami East constitute the geologic entity at Miami, Ariz., and San Manuel and Kalamazoo constitute the entity at San Manuel, Ariz.

Grades and tonnages for the massive sulfide and strata-bound copper deposits were obtained from Manifile (Laznicka, 1973). The strata-bound deposits were selected by using the Manifile "similarity type" CPBT (Copperbelt deposits, Africa-U.S.S.R.). Only African strata-bound deposits were used because other known strata-bound deposits are few and are in different economic and possibly different geologic environments. Different economic conditions would alter the cutoff grades (lowest grade of blocks of ore considered in reserve estimates), which in turn would change the average grades and the tonnages. Other Manifile "similarity types"— MSCP (massive copper pyrites), MSCZ (massive sulfide copper-zinc), and KRKO (Kuroko (Japan) deposits)—were combined to provide the massive sulfide grades and tonnages.

Data from the porphyry copper deposits came from many sources. Among them are prospectus offerings of American Smelting and Refining Co. (1969), Kennecott Copper Corp. (1971), Newmont Mining Corp. (1969), Phelps Dodge Corp. (1970), Anaconda Co. (1968), and U.S. Smelting Refining and Mining Co. (1968); a book on porphyries by Sutulov (1974); and various issues of "Metals Sourcebook" (Metals Week, 1973–74). Additional grade and tonnage estimates were made by U.S. Geological Survey geologists familiar with individual deposits.

An attempt was made to obtain estimates of the grades and tonnages that ultimately might be recovered from each deposit. In general, this required using the tonnage and grade estimates associated with the lowest cutoff grade available. This effort was successful for the porphyries in the United States for which the authors have confidence in the estimates used. Most of the porphyries in Canada and in the southwest Pacific have only recently been drilled; a potential exists for higher tonnages as development proceeds. The earlier developed porphyries of South America have been operating with relatively high cutoff grades, which means that the average operating grades are high. Because of their very large size, some of the South American porphyries have not yet been drilled out, and estimates of grades and tonnages at low cutoff grades are not available at this time.

Although the difference is cutoff grades in diferent regions affects the average grades, reducing the cutoff grades to a common base would not completely remove the differences in average grades and tonnages. For example, if the average grades and tonnages of all the porphyry copper deposits of North and South America were estimated using a 0.2 percent copper cutoff grade, the South American porphyries would probably still have the highest average grade and tonnage and the Canadian and Alaskan porphyries would still have the lowest average grade and tonnage. Evidence for this statement may be found in the relatively constant difference between the cutoff grade and the average grade within a given porphyry; the difference is relatively large for the South American porphyries and tends to become smaller for porphyries to the north.

UNIVARIATE STATISTICAL ANALYSIS

The purpose of univariate statistical analysis is to determine which theoretical distribution models best describe the individual distributions of the average grade and tonnage of the three types of copper deposits considered. In particular, the ability of normal and lognormal distribution models to describe distributions was examined. The adequacy with which these two theoretical frequency distributions fit the observed grade and tonnage frequency distributions was determined by using both beta ($\sqrt{b_1}$ and b_2) and chi square goodness-of-fit statistics. The beta statistics describe the shape of the frequency distribution: For the normal distribution, $\sqrt{b_1}$, a measure of asymmetry, has an expected value of 0.0, and b_2, a measure of peakedness, has an expected value of 3.0. The chi square statistic measures the class-to-class departure of observed distribution from the theoretical distribution model from which the observed distribution is hypothesized as being a sample. The beta statistics and the chi square statistics provide complementary information about the adequacy of fit, lesser weight generally being given to chi square statistics because of the arbitrary decisions that must be made when an observed frequency distribution is constructed (Shapiro and others, 1968).

Average grade and tonnage data were obtained from 267 copper deposits. Of these, 146 are massive sulfide deposits, 103 are porphyry deposits, and 18 are strata-bound deposits. Frequency distributions of tonnage and grade were constructed, and summary and goodness-of-fit statistics were computed for each type of deposit. Within the 103 porphyry deposits, 4 subdivisions were recognized which were based upon the metallogenic province within which the deposits occurred. The summary statistics are shown in tables 1 and 2, and goodness-of-fit statistics, in table 3.

Examination of table 1 shows that the African strata-bound deposits have the highest average grade (3.78 percent Cu), followed closely by the massive sulfide deposits, which have an average grade of 2.92 percent copper. The porphyry deposits have an average grade of 0.63 percent Cu, which is nearly one-fifth that of the massive sulfide deposits. Within the porphyry deposits, the average grade ranges from 0.49 percent copper for the Canadian deposits to 0.99 percent copper for the South American deposits. The average grades for the United States-Mexico deposits (0.59 percent copper) and the southwest Pacific deposits (0.52 percent copper) are close to the average grade of the Canadian deposits.

The massive sulfide deposits are far more variable in average grade than the other type of deposits; they have a standard deviation of 2.35 percent copper. This is a consequence of the large skewness in the distribution of grade of these deposits. The standard deviation of the average grades of the strata-bound deposits is 1.18 percent copper, which is only half that of the massive sulfide distribution. The standard deviations of three of the four subclasses of porphyry deposits range only from 0.12 percent copper to 0.17 percent copper. The fourth member of this class of deposits (South American) has a standard deviation (0.36 percent copper) more than twice that of any of the other members of this class.

Porphyry copper deposits contain an average of 548 million tons of ore (table 2), about six times as much ore as that contained in the strata-bound deposits, which average 91 million tons. Massive sulfide deposits contain an average of only 10.3 million tons of ore by comparison, or nearly an order of magnitude less than that contained in the average

TABLE 1.—*Summary statistics for the average grades of copper deposits*

Type of deposit	Number of deposits	Arithmetic data			Logarithmic data	
		Mean grade	Standard deviation	Median grade	Mean, $\log_{10}$ of grades	Standard deviation, $\log_{10}$ of grades
Porphyry:						
Canada	21	0.0049	0.0017	0.0047	—2.331	0.147
United States and Mexico	38	.0059	.0014	.0057	—2.243	.101
South America	20	.0099	.0036	.0093	—2.033	.160
Southwest Pacific	24	.0052	.0012	.0051	—2.296	.114
World	103	.0063	.0027	.0059	—2.233	.162
Massive sulfide	146	.0292	.0235	.0229	—1.640	.303
Strata-bound	18	.0378	.0118	.0362	—1.442	.132
All	267	.0210	.0213	.0140	—1.855	.392

TABLE 2.—*Summary statistics for the tonnage of copper deposits*

Type of deposit	Number of deposits	Arithmetic data				Logarithmic data	
		Mean (millions of metric tons of ore)	Median (millions of metric tons of ore)	Mean (thousands of metric tons of copper)	Median (thousand of metric tons of copper)	Mean, $\log_{10}$ of metric tons	Standard deviation, $\log_{10}$ of metric tons
Porphyry:							
Canada	21	245	177	1,210	824	8.247	0.354
United States and Mexico	38	815	338	4,781	1,932	8.529	.629
South America	20	773	347	7,622	3,214	8.540	.610
Southwest Pacific	24	203	120	1,058	608	8.080	.436
World	103	548	234	3,452	1,368	8.369	.565
Massive sulfide	146	10.3	2.26	301	52	6.354	.828
Strata-bound	18	91	41.4	3,453	1,496	7.617	.690
All	267	223	16.5	4,679	230	7.217	1.208

TABLE 3.—*Beta and chi square goodness-of-fit statistics*

[*N*, number of deposits; X^2, chi square value; df, degrees of freedom; NS, not significant; *, significant at 5-percent level; **, significant at 1-percent level]

Type of deposit		Mean grade						Tonnage, logarithmic		
		Arithmetic			Logarithmic					
	N	X^2(df)	$\sqrt{b_1}$	b_2	X^2(df)	$\sqrt{b_1}$	b_2	X^2(df)	$\sqrt{b_1}$	b_2
Porphyry:										
Canada	21	14.1 ** (2)	1.34 *	4.95 *	5.9 NS (2)	—0.26 NS	5.28 *	2.3 NS (2)	0.25 NS	2.72 NS
United States and Mexico	38	2.5 NS (4)	.75 **	3.97 NS	1.4 NS (4)	.02 NS	2.96 NS	12.4 * (4)	—.17 NS	2.42 NS
South America	20	2.0 NS (2)	.67 NS	2.60 NS	1.0 NS (2)	—.19 NS	3.14 NS	1.8 NS (2)	—.15 NS	2.10 NS
Southwest Pacific	24	4.5 NS (2)	.43 NS	5.34 *	11.4 ** (2)	—1.40*	8.08*	2.5 NS (2)	.43 NS	2.78 NS
World	103	39.7 ** (6)	1.91 **	7.49 **	16.0 ** (6)	.35 NS	4.47 **	21.9 ** (6)	.24 NS	2.49 NS
Massive sulfide	146	73.2 ** (8)	2.37 **	10.02 **	16.2 * (8)	—.04 NS	3.67 *	10.1 NS (8)	—.20 NS	2.96 NS
Strata-bound	18	3.4 NS (2)	.89 *	3.78 NS	1.1 NS (2)	.09 NS	2.77 NS	7.2 * (2)	—.60 NS	2.18 NS
All	267	202.3 ** (8)	2.50 **	11.70 **	69.3 ** (8)	.20 NS	2.19 **	24.9 ** (8)	—.18 NS	2.26 **

strata-bound deposit. Nearly the same relative differences in tonnages between deposit types were found when the median tonnage is used as a measure of the "center of gravity" of the distributions. Strata-bound deposits contain a median 41.4 million tons, and the massive sulfides have a median of 2.26 million tons. When considering the distribution of the tonnage of ore in each type of deposit, the median is a more appropriate measure of the center of gravity because of the large skewness toward the high tonnage tail in each of these distributions.

African strata-bound deposits have the largest quantity of contained copper—a median of 1,496,000 tons. The porphyry deposits have a median that is slightly less—1,368,000 tons—and the massive sulfide deposits contain even less copper by comparison—a median of 52,000 tons. Within the four subclasses of porphyry deposits, the median metal content ranges from 608,000 tons for the southwest Pacific deposits to 3,214,000 tons for the South American deposits. The United States-Mexico deposits have a median of 1,932,000 tons of copper metal, which is more than twice as much as the median for the Canadian deposits but only a little more than half that for the South American deposits.

The process of selecting an appropriate theoretical distribution model to describe the observed grade and tonnage frequency distributions for each of the three types of copper deposits was based upon statistical tests of the beta and chi square goodness-of-fit statistics. The results of these tests are shown in table 3. With the exception of the southwest Pacific porphyry deposits, the lognormal distribution model was found to be superior to the normal distributions in describing the observed distribution of mean grade and tonnage.

Each of the observed distributions of tonnage of ore studied was found to be highly skewed toward high tonnages, and, as a consequence, the normal model does not provide an adequate fit to the observed data. The lognormal model, on the other hand, was found to fit each of the observed tonnage distributions rather well. For each category shown in table 3, column 1, the skewness of the observed tonnage distribution was within the expected range for a sample from a lognormal population, and in only one category did the peakedness depart significantly from the lognormal model. In four of the eight categories, the chi square goodness-of-fit statistics were significant. However, we give less weight to the chi square test statistic because the statistic will produce varying results depending upon the choice of class limits. The lognormal distribution is accepted as an adequate model for the distribution of tonnage of ore in deposits from each category of deposit.

As a result of the above analysis and the assumption that the observed data can be regarded as randomly drawn from their respective parent populations, the lognormal models provide not only an adequate description of tonnage of ore in yet-to-be-discovered deposits of the three types of deposits studied, but also offer an adequate description of their mean grades. An additional benefit of the above results is that the correlation between the logarithms of the mean grade and tonnage in these deposits can be tested statistically.

CORRELATIONS BETWEEN GRADE AND TONNAGE

Among the problems that must be resolved before resource models can be constructed is the relationship between the pairs of variables being examined. In this paper, the pairs of variables are the average grades and the tonnages of the copper deposits in each of the sets of deposit types under consideration; the degree to which these variables vary together is tested. The degree of association or interdependence of the pairs of variables is examined by means of the correlation coefficient for each set of samples. The values of the correlation coefficient can range between minus one and plus one, a perfect linear relationship being indicated by a minus one or plus one value, and complete linear independence indicated by zero. In this paper, the sample correlation coefficients are tested in table 4 against the null hypothesis that the population of grades and tonnages has zero correlation. The frequency distribution of the pairs of logarithmic variables examined in the last section closely approximate the bivariate normal distribution necessary for the significance tests of the null hypothesis.

TABLE 4.—*Correlation coefficients between average copper grade and total tonnage*

[NS, not significant; **, significant at the 1-percent level]

Type of deposit	Number of deposits	Correlation coefficient	
		Arithmetic data	Logarithmic data
Porphyry:			
Canada	21	−0.16NS	−0.22NS
United States and Mexico	38	.00NS	−.09NS
South America	20	−.07NS	−.17NS
Southwest Pacific	24	−.05NS	−.07NS
World	103	.09NS	.05NS
Massive sulfide	146	−.13NS	−.42**
Strata-bound	18	−.10NS	−.19NS
All	267	−.22**	−.67**

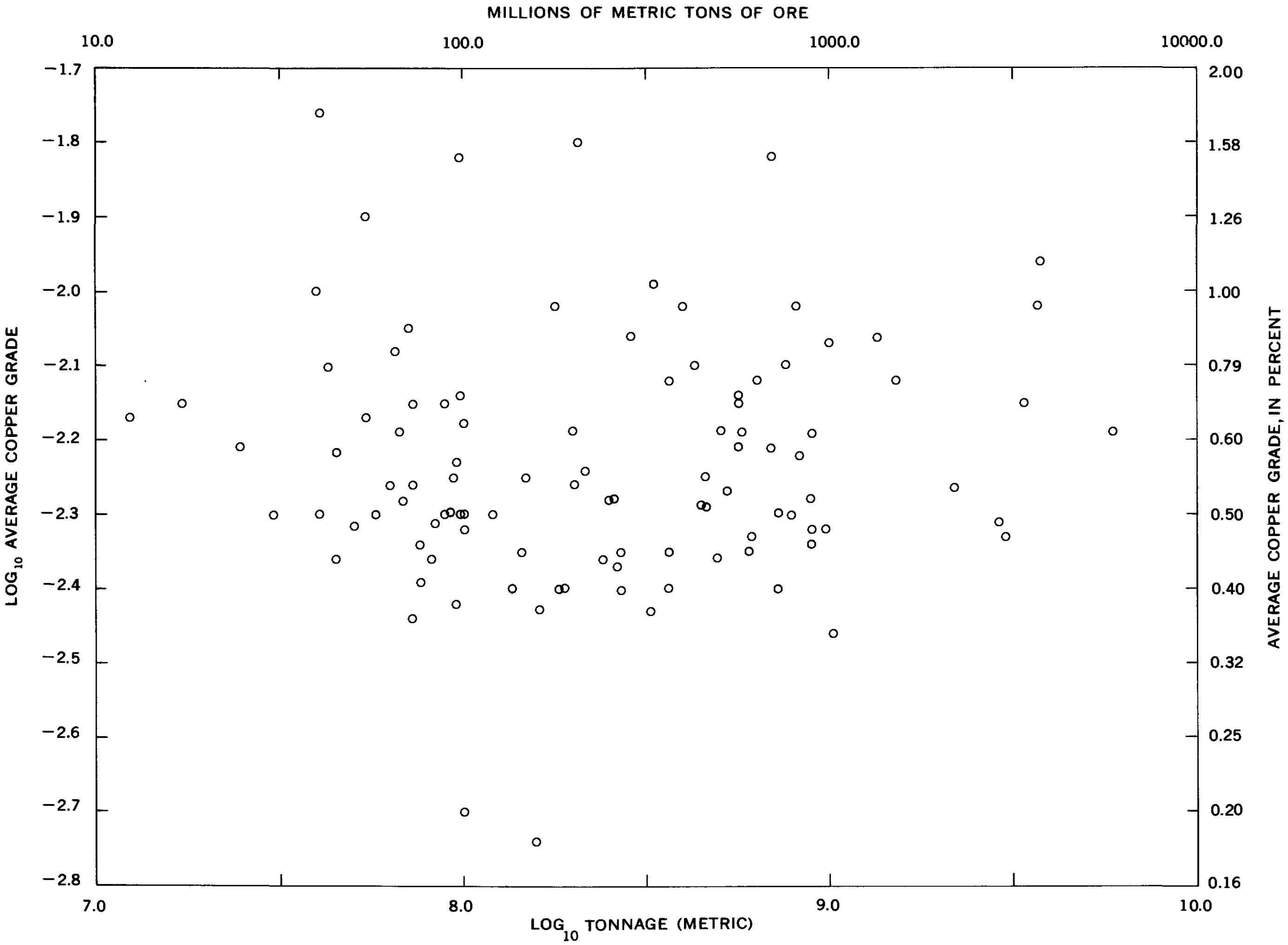


FIGURE 1.—Grades and tonnages for porphyry copper deposits.

Sample correlation coefficients calculated for both the arithmetic data and the logarithmic data for each group of porphyry coppers and for all the porphyries together provide no basis for rejecting the null hypothesis of zero correlation between average grade and tonnage (fig. 1). In fact, less than 5 percent of the variation of tonnage is explained by the average grade for these deposits. These results also hold for the strata-bound deposits (fig. 2).

The correlation coefficients for both the massive sulfide deposits (fig. 3) and the combination of all deposits are negative and highly significant (table 4). This suggests a significant negative relationship between grade and tonnage for both groups, although it should be noted that the combination of all deposits represents not only a mixture of geologic types of deposits, but a statistical mixture as reflected in the significant departures of grade and tonnage from the lognormal distribution. Additional statistical analyses were performed but not included on two of the subgroups of massive sulfides; logarithms of the grades and tonnages from the Manifile "similarity types" massive copper pyrites and massive sulfide copper-zinc (see p. 1–2) each had significant negative correlations.

The negative relationship between grade and tonnage for the massive sulfide deposits may be accounted for by the fact that some deposits include a combination of low-tonnage high-grade massive ores and large-tonnage low-grade stockwork and disseminated ores. These ores, though genetically related, represent a mixed population with respect to the tonnage-grade relationship.

DISCUSSION AND CONCLUSIONS

The independence of grade and tonnage for porphyries is convenient for modeling of grades and tonnages of yet unmined deposits. As the grades and tonnages are essentially lognormally distributed for

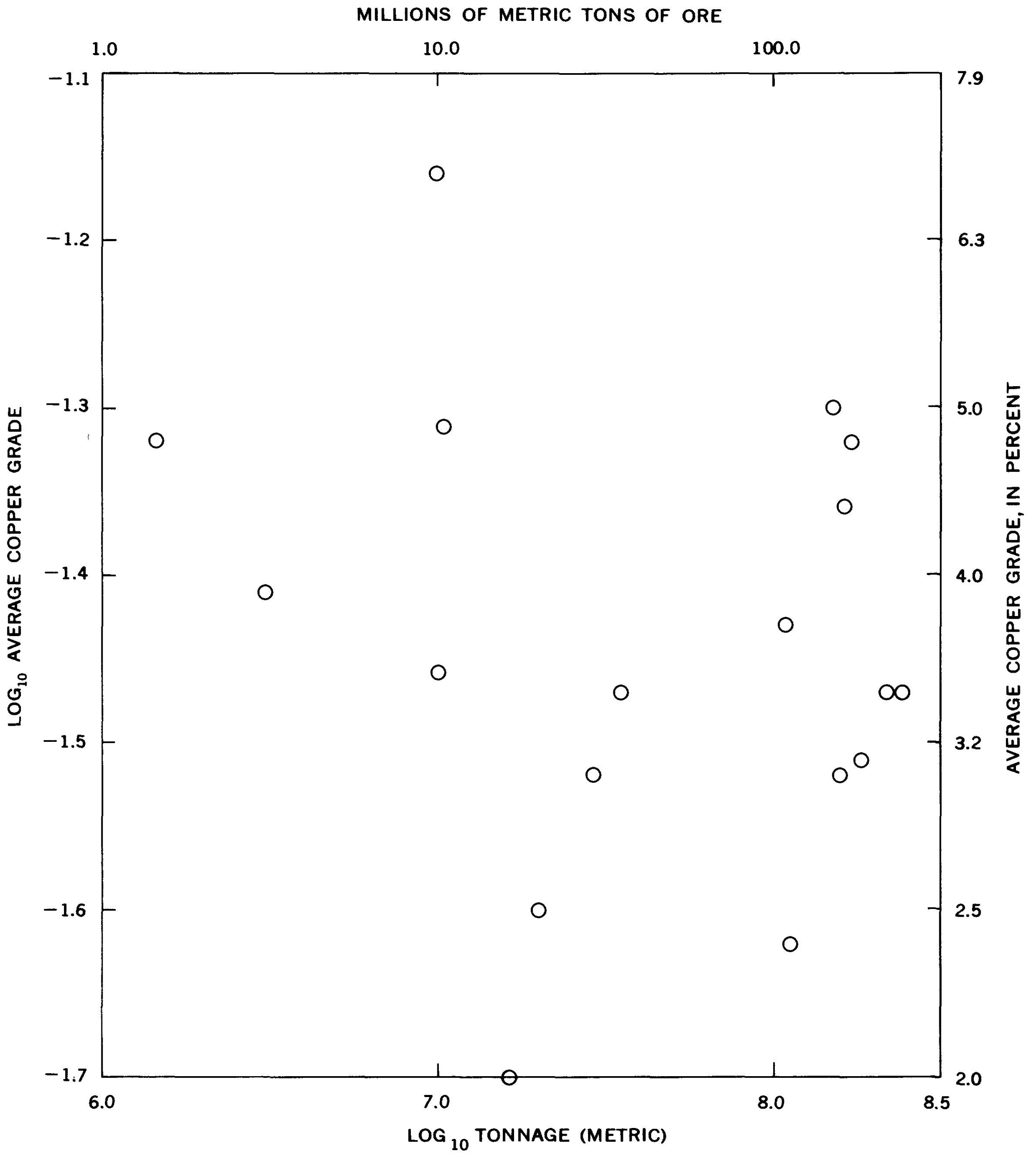


FIGURE 2.—Grades and tonnages for African strata-bound copper deposits.

the porphyries, the calculation of the probability of the occurrence of any particular range of grades or tonnages, given that a porphyry exists, is an easy task. Because of the independence of grade and tonnage, the probability of a deposit falling in particular ranges of grades and tonnages is simply the product of the probabilities of the range of grades and of the range of tonnages. For example, suppose it is desirable to find the probability of a porphyry having a very low grade and a very large tonnage. The probability of a very low grade, say less than two standard deviations below the mean (less than 0.28 percent copper), is equal to 0.023 from tables of the areas of the normal curve (Dixon and Massey, 1957). The probability of a very large tonnage, say more than three standard deviations above the mean (greater than 11.59 billion tons), is 0.0013 from the normal curve tables. Thus, the probability of a porphyry having a grade less than 0.28 percent and a tonnage greater than 11.59 billion tons is 0.023 ×

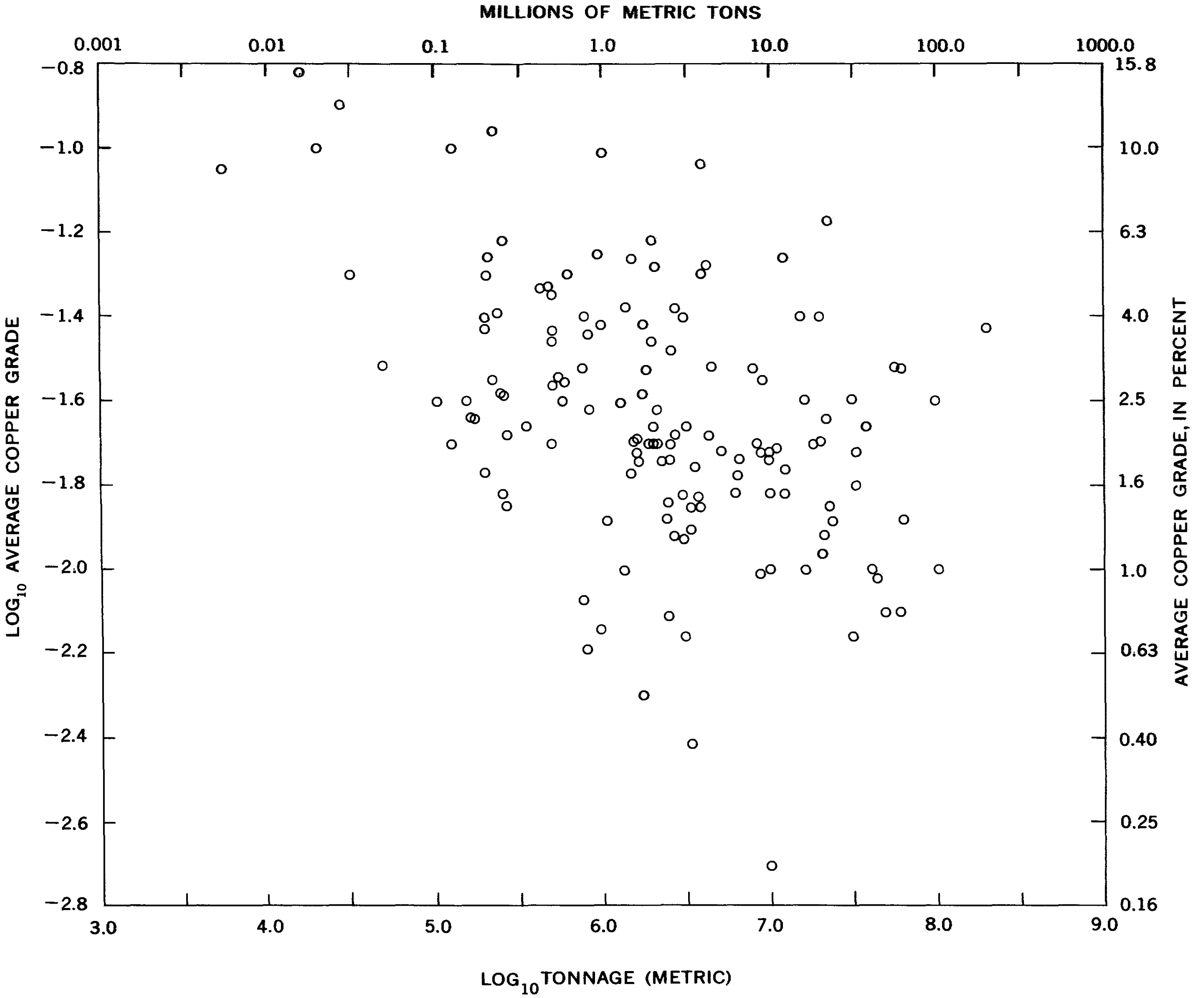


FIGURE 3.—Grades and tonnages for massive sulfide deposits.

0.0013 or 0.00003; that is, if 33,000 deposits were discovered, only one of them would be likely to have these characteristics—a very unlikely event indeed. It is interesting to note that if such a deposit exists, it contains about 32 million tons of copper, which is about the amount contained in the largest known porphyries, and it would require the moving of about 4 cubic miles of rock to mine it.

If improvements in technology allow mining of lower and lower grade porphyry deposits, the most probable tonnage of these new deposits will be roughly the same as those presently being exploited; thus, each deposit will contain less copper. D. P. Harris (oral commun., 1973) has suggested that low-grade deposits of median tonnage are more abundant than those of higher grades. Although no geologic evidence is presently available to support this assumption, it represents an important area for future investigation.

The lack of correlation of tonnage and grade for both the strata-bound and porphyry deposits has implications not only for quantitative modeling, such as mentioned above, but also qualitative modeling. Qualitative modeling is often used by those considering the future supply of natural resources, and usually an assumption of a negative correlation between grade and tonnage is implicit in their discussions. The above analysis does not support this view. Such untested beliefs could have arisen from several sources including the trend through time of lower average copper grades mined each year, which is related to improvements in technology, changing deposit types, and the tendency for porphyries to have richer grades in the earliest mined areas. Another possible source of these beliefs could come from misinterpretation of Lasky's (1950) work on the grade and tonnage relationship Lasky found that within porphyries the cumulative tonnage increases at a constant geometric rate as the grade decreases at an arithmetic rate. The method of using cumulative tonnage could be applied across porphyry deposits, and the results would be consistent with Lasky's results (John Whitney, written commun., 1974). Lasky's cumulative contained copper curves become flat at a point that he called zero cutoff grade. Zero cutoff grade represents the outer limit of the effects of the special geologic conditions that gave rise to the ore deposit. Copper content does not fall to zero at this limit but tends to approach average abundance of copper in the Earth's crust.

In conclusion, an inverse relationship between grade and tonnage is often a hidden assumption in mineral-resource supply models. Use of such models for policy decisions could have a devastating effect on the orderly supply of minerals if large tonnage-very low grade deposits do not exist.

From the inverse relationship between average grade and tonnage shown by the mixture of three deposit types, it is tempting to extrapolate the existence of large-tonnage very low grade deposits, and it can be reasoned that such deposits can supply sufficient copper for our future needs. Such an extrapolation is misleading for statistical and geological reasons. It is statistically erroneous to extrapolate on the basis of a mixed population, especially because the distributions of tonnages and grades in the largest tonnage lowest grade (porphyry) subset of the population show that large-tonnage very low grade deposits are rare occurrences. In addition, discussion with industry geologists familiar with porphyry deposits indicates that a large number of such deposits is not being held in company inventories at present.

If large-tonnage very low grade deposits exist, they probably will not resemble any of the three important types presently exploited. Discovery of such unconceived resources will require continuing research on a broadly based spectrum of geologic phenomena.

REFERENCES CITED

American Smelting and Refining Co., 1969, [Prospectus proposing a merger with Pennzoil United, Inc., January 1969]: 66 p.

Anaconda Co., 1968 [Prospectus offering debentures, Nov. 1968]: 37 p

Anderson, C. A., 1969, Massive sulfide deposits and volcanism: Econ. Geology, v. 64, no. 2, p. 129–146.

Dixon, W. J., and Massey, F. J., Jr., 1957, Introduction to statistical analysis [2d ed.]: New York, McGraw-Hill, 488 p.

Kennecott Copper Corp., 1971, [Prospectus offering debentures, April 1971]: 14 p.

Lasky, S. G., 1950, How tonnage and grade relations help predict ore reserves: Eng. and Mining Jour., v. 151, no. 4, p. 81–85.

Lazinicka, Peter, compiler, 1973, Manifile; the University of Manitoba file of nonferrous metal deposits of the world: Manitoba Univ., Dept. Earth Sci., Centre Precambrian Studies Pub. 2, 3 v.: Pt. 1, 533 p.; Pt. 2, v. 1, 298 p.; Pt. 2, v. 2, 767 p.

Lowell, J. D., and Guilbert, J. M., 1970, Lateral and vertical alteration-mineralization zoning in porphyry ore deposits: Econ. Geology, v. 65, no. 4, p. 373–408.

Metals Week, 1973–74, Metals sourcebook: New York, McGraw-Hill, [weekly pub.].

Meyer, Charles, Shea, E. P., and Goddard, C. C., Jr., 1968, Ore deposits at Butte, Montana, *in* Ridge, J. D., ed., Ore deposits of the United States, 1933–1967 (Graton-Sales Volume), v. 2: New York, Am. Inst. Mining. Metall., and Petroleum Engineers, p. 1373–1416.

Moolick, R. T., and Durek, J. J., 1966, The Morenci district, *in* Titley, S. R., and Hicks, C. L., eds., Geology of the porphyry copper deposits, southwestern North America: Tucson, Ariz., Arizona Univ. Press, p. 221–231.

Newmont Mining Corp., 1969, [Prospectus proposing a merger with Magma Copper Co., May 1969]: 59 p.

Phelps Dodge Corp., 1970, [Prospectus proposing a merger with Western Nuclear, Inc., October 1970]: 8 p.

Shapiro, S. S., Wilk, M. B., and Chen, H. J., 1968, A comparative study of various tests for normality: Am. Stat. Assoc. Jour., v. 63, no. 324, p. 1343–1372.

Sutulov, Alexander, 1974, Copper porphyries: Salt Lake City, Utah, Univ. Utah Printing Services, 200 p.

Tatsumi, Tatsuo, and Watanabe, Takeo, 1971, Geological environment of formation of the Kuroko-type deposits: Soc. Mining Geology Japan, Spec. Issue 3, p. 216–220.

U.S. Smelting Refining and Mining Co., 1968, [Prospectus offering debentures, Feb. 1968]: 8 p.

Geochemical Exploration Techniques Applicable in the Search for Copper Deposits

By MAURICE A. CHAFFEE

GEOLOGY AND RESOURCES OF COPPER DEPOSITS

GEOLOGICAL SURVEY PROFESSIONAL PAPER 907-B

A compilation of proved and untried geochemical sampling media and techniques that may be useful in the search for new copper deposits

UNITED STATES GOVERNMENT PRINTING OFFICE, WASHINGTON : 1975

CONTENTS

ILLUSTRATIONS

GEOCHEMICAL EXPLORATION TECHNIQUES APPLICABLE IN THE SEARCH FOR COPPER DEPOSITS

By Maurice A. Chaffee

ABSTRACT

Geochemical exploration is an important part of copper-resource evaluation. A large number of geochemical exploration techniques, both proved and untried, are available to the geochemist to use in the search for new copper deposits.

Analyses of whole-rock samples have been used in both regional and local geochemical exploration surveys in the search for copper. Analyses of mineral separates, such as biotite, magnetite, and sulfides, have also been used.

Analyses of soil samples are widely used in geochemical exploration, especially for localized surveys. It is important to distinguish between residual and transported soil types. Orientation studies should always be conducted prior to a geochemical investigation in a given area in order to determine the best soil horizon and the best size of soil material for sampling in that area. Silty frost boils, caliche, and desert varnish are specialized types of soil samples that might be useful sampling media.

Soil gas is a new and potentially valuable geochemical sampling medium, especially in exploring for buried mineral deposits in arid regions. Gaseous products in samples of soil may be related to base-metal deposits and include mercury vapor, sulfur dioxide, hydrogen sulfide, carbon oxysulfide, carbon dioxide, hydrogen, oxygen, nitrogen, the noble gases, the halogens, and many hydrocarbon compounds.

Transported materials that have been used in geochemical sampling programs include glacial float boulders, glacial till, esker gravels, stream sediments, stream-sediment concentrates, and lake sediments. Stream-sediment sampling is probably the most widely used and most successful geochemical exploration technique.

Hydrogeochemical exploration programs have utilized hot- and cold-spring waters and their precipitates as well as waters from lakes, streams, and wells. Organic gel found in lakes and at stream mouths is an unproved sampling medium. Suspended material and dissolved gases in any type of water may also be useful media. Samples of ice and snow have been used for limited geochemical surveys.

Both geobotanical and biogeochemical surveys have been successful in locating copper deposits in many parts of the world. Micro-organisms, including bacteria and algae, are other unproved media that should be studied.

Animals can be used in geochemical-prospecting programs. Dogs have been used quite successfully to sniff out hidden and exposed sulfide minerals. Termite mounds are commonly composed of subsurface material, but have not as yet proved to be useful in locating buried mineral deposits. Animal tissue and waste products are essentially unproved but potentially valuable sampling media. Knowledge of the location of areas where trace-element-associated diseases in animals and man are endemic, as well as a better understanding of these diseases, may aid in identifying regions that are enriched in or depleted of various elements, including copper.

Results of analyses of gases in the atmosphere are proving valuable in mineral-exploration surveys. Studies involving metallic compounds exhaled by plants into the atmosphere, and of particulate matter suspended in the atmosphere are reviewed; these methods may become important in the future.

Remote-sensing techniques are useful for making indirect measurements of geochemical responses. Two techniques applicable to geochemical exploration are neutron-activation analysis and gamma-ray spectrometry. Aerial photography is especially useful in vegetation surveys. Radar imagery is an unproved but potentially valuable method for use in studies of vegetation in perpetually clouded regions.

With the advent of modern computers, many new techniques, such as correlation analysis, regression analysis, discriminant analysis, factor analysis, cluster analysis, trend-surface analysis, and moving-average analysis can be applied to geochemical data sets. Selective use of these techniques can provide new insights into the interpretation and understanding of geochemical data that would not be possible without the use of computers.

INTRODUCTION

An important part of our fund of knowledge of copper resources must include techniques for the exploration for new copper deposits. Among the techniques, those using geochemistry are becoming increasingly important.

For this report I reviewed much of the geochemical literature. I have selected for discussion primarily those papers that deal with geochemical exploration for copper deposits in the widely differing geologic and climatic environments found on earth. In addition to published reports, I have also included, wherever pertinent, information on geochemical prospecting investigations currently being conducted by scientists in the U.S. Geological Survey. I have also suggested some unproved geochemical exploration techniques that might be useful in the search for new copper deposits.

No attempt has been made to compare and evaluate the various studies described in this report; too many variations exist to permit valid comparisons. Undoubtedly, some techniques have been overlooked; other methods, developed by private organizations, have not been documented in the literature, either because of their success or because of their lack of it.

Those readers interested in more complete discussions of the large geochemical prospecting bibliography should refer to the books by Ginzburg (1960), Hawkes and Webb (1962), and Levinson (1974). A review article dealing exclusively with porphyry copper deposits has also been published recently (Coope, 1973).

GEOCHEMICAL SAMPLING MEDIA

ROCKS AND MINERALS

Geochemical sampling of rocks is the most basic type of sampling because, ultimately, it is the rock material of mineral deposits that must be studied and mined. Several types of rock samples are used in exploration. The two main types are (1) whole-rock samples and (2) mineral-separate samples.

Whole-rock samples can be used to provide information about the abundance and distribution of elements or groups of elements. Variations in the concentrations of minor elements can be statistically interpreted to define mineralized areas on any scale. On a regional scale, geochemical studies alone, or in combination with geologic and(or) geophysical data, can be used to define copper-rich metallogenic provinces or districts. On a local scale, whole-rock analyses can be used for detailed studies to locate individual deposits or extensions of known deposits.

The use of bedrock geochemical surveys has generally not found favor among geochemists for several reasons. Rock bodies have normal variations in trace elements that can be ascribed to many causes other than mineral deposits. Thus, it is difficult to collect representative samples that can be economically evaluated purely on the basis of chemical abundances. Also, bedrock samples have not undergone mechanical dispersion that might enlarge a potential target.

Whole-rock analyses of bedrock samples can be useful in the search for large copper ore bodies such as porphyry-, magmatic segregation-, or bedded-type deposits. A comparison of the trace elements in samples of rock taken from intrusive rocks throughout a region can be used as a regional exploration guide. It is important, therefore, in this type of study that the samples collected from a given intrusive rock are as representative as possible of the character of the entire rock body.

Putnam and Burnham (1963) used whole-rock analyses in a regional study of a part of the Arizona copper province. They found that samples from plutonic bodies associated with known copper mineralization contained higher copper concentrations than did those from plutonic bodies not associated with known copper deposits. Most of the copper was found to occur in the ferromagnesian and sulfide minerals.

Other applications of whole-rock trace-element chemistry as a regional exploration technique in the search for copper were carried out in British Columbia by Warren and Delavault (1960, 1969). These authors used hot aqua regia for extraction, and found that copper and zinc concentrations in the samples from both plutonic and volcanic rock bodies indicated the presence of genetically associated copper mineralization nearby. High copper-zinc ratios (>0.35 for volcanic rocks and >0.20 for plutonic rocks) provided further information as to the favorability of certain areas.

In a study undertaken by the Geological Survey of Canada, Sakrison (1971) described another regional geochemical survey using whole-rock samples. In that survey, copper concentrations in bedrock samples from a large area of the Canadian Shield were determined. A number of areas anomalously high in copper were found, some of which correlated with known mineralized rock bodies.

Similar surveys using whole-rock samples may be useful for appraising the potential of any region thought to contain large strata-bound copper deposits. Many regions contain a thick stratigraphic section composed of many different rock types. Widely differing rock types can be expected to contain large normal variations in the abundances of many chemical elements. Ideally, it would be desirable to select rock material from only one formation or bed as a representative sample of the entire stratigraphic section at a given outcrop of the section. This restricted sampling scheme would significantly reduce the number of samples needed, and would also require sampling of only one lithology, thereby reducing or eliminating the complication of any chemical variability caused by sampling of different lithologies with different normal abundances of various trace elements. Results of sampling of selected beds or formations should be able to show trends in trace-element content and also to indicate those geologic formations or beds that are most likely to contain copper deposits. My experience in the vicinity of the Vekol porphyry copper-molybdenum deposit near Casa Grande, Ariz., indicated that this technique of sampling a particular stratigraphic unit, when applied on a regional basis, could delineate localities containing epigenetic copper minerals in favorable sedimentary host formations. In my study, rock samples showing no visible signs of hydrothermal alteration were collected from formations in a Paleozoic sequence that cropped out over a large region in the vicinity of the Vekol deposit. Anomalous copper concentrations were detected in samples from several formations over 3 km (about 2 mi) away from the deposit. Copper concentrations generally increased in samples taken progressively closer to the deposit; maximum concentrations were found in samples directly over the deposit. Anomalous molybdenum concentrations were detected in only two of the formations present in the region, and then only in those samples collected directly over the Vekol deposit; the same formations in other localities did not contain anomalous amounts of molybdenum.

At Jerome, Ariz., primary copper from Precambrian ore deposits was mobilized by weathering and deposited as syngenetic copper in the superjacent Cambrian sandstone that is present at the base of a thick Paleozoic sedimentary sequence. Huff (1955) collected and analyzed samples of this basal sandstone unit and demonstrated that this formation contained anomalous concentrations of copper as much as 3 km (about 2 mi) away from the known ore deposits.

Whole-rock analyses can also be used on a local scale to identify individual deposits in a district or to find extensions of known deposits. Most large ore bodies have boundaries that are economic rather than mineralogic; that is, their boundaries are based on a grade of ore that is economic and not on a sudden disappearance of a particular element. Looked at another way, most large ore bodies have dispersion aureoles of various elements. The geochemical expression of a hypothetical porphyry deposit of the type common to the southwestern United States was reviewed by Jerome (1966). He noted that gold, silver, and molybdenum are commonly found enriched in the copper-ore zone, a fact generally known. On the basis of analyses of ores, gossans, leached cappings, smelter products, tailings, and concentrates from copper deposits, Jerome concluded that antimony, arsenic, bismuth, cobalt, indium, nickel, rhenium, selenium, tellurium, tin, and vanadium may also be enriched in or around the copper-ore zone. My investigations confirm, at least in part, Jerome's findings. Most of the elements mentioned by Jerome have been detected in the ore zone of the Kalamazoo ore body near San Manuel, Ariz. Distributions of the trace-element concentrations relative to the known ore body indicate that many trace elements form either positive or negative primary dispersion aureoles around the copper deposit. Perhaps a statistical study of the concentrations of a group of trace elements in rock samples, together with their locations relative to this known porphyry copper ore body, can be used to predict the direction to the copper ore from any point within the host-rock body. If this type of study is successful and if a geochemical model for the trace-element aureoles can be derived for this deposit, then it may be possible to use geochemical data from sample sites near other similar but seemingly barren plutonic rocks to predict (1) the presence or absence of copper deposits at depth and (2) the possible location of a blind deposit.

Studies made of trace elements in rock samples near volcanogenic copper deposits in the Soviet Union revealed dispersion patterns of the ore metals, and such volatile elements as iodine, extending as far as 140 m (460 ft) from known ore bodies (Rubo, 1969). This study, when considered in conjunction with previously described studies, indicates that the use of trace-element zoning patterns in bedrock may be valid as a geochemical-exploration technique for nearly any type of copper deposit.

Analysis of mineral separates is another approach to rock sampling. In their regional study of plutons in Arizona, Putman and Burnham (1963) noted that essentially all of the zinc and much of the copper in their rock samples came from the ferromagnesian minerals. Even more interesting is their observation that "in every sample in which chalcopyrite is presumed to be present, the coexisting biotite has a relatively high copper content, usually above the average copper content of biotites from other samples" (Putman and Burnham, 1963, p. 72). These authors concluded that the biotite and the chalcopyrite came from the same magma. Studies of the concentrations of copper in biotites from major copper districts in Nevada, Utah, Montana, and Arizona have since confirmed the close relationship between copper-rich biotite and copper-rich rock bodies (Parry and Nackowski, 1963; Al-Hashimi and Brownlow, 1970; Lovering and others, 1970).

A number of investigations of the trace-element content of magnetite have been made. Hamil and Nackowski (1971) demonstrated that the concentration of copper in magnetites was not a good criterion for locating porphyry-copper intrusive rocks. In contrast, they found that low concentrations of titanium and zinc in magnetite were better indicators of copper-related intrusive rocks. In my experience, the lack of correlation of concentrations of copper in magnetites with intrusive rock bodies enriched in copper-bearing minerals may be caused by the inability of the person making the study to interpret properly the age of the magnetite relative to the age of the copper-bearing minerals. The magnetite may not be cogenetic with the economic copper-bearing minerals. When this latter situation holds true, the trace-element content of the magnetite (or possibly of other mineral separates) probably bears no useful relationship to the presence or absence of copper in the intrusive body.

In another study, Smith (1970) determined the trace-element content of heavy-mineral fractions from samples collected from a group of plutons in the Plumas copper belt in northern California. He found that the highest copper concentrations were restricted to samples collected from those plutons that contained the copper deposits that produced the largest tonnages of copper ore in the region.

The analysis of trace elements in metal sulfide concentrates derived from whole-rock samples has been used as a means of defining metallogenic provinces for several elements. Burnham (1959) analyzed more than 500 samples of chalcopyrite and sphalerite from 172 mining districts widely scattered throughout the southwestern United States. His data showed closely coincident zones or belts enriched in such elements as tin, silver, cobalt, nickel, indium, gallium, and germanium. The belts defined by the trace-element content of sphalerite are considered by Burnham to coincide with the trends of known copper belts.

The rhenium concentration in samples of molybdenite from porphyry copper deposits was shown to differ markedly from its concentration in samples of molybdenite from other types of deposits (Giles and Schilling, 1972). These differences in concentration suggest that the abundance levels of trace elements in ore minerals may be a useful guide in evaluating porphyry copper-molybdenum deposits and possibly other types of copper deposits.

Undoubtedly many other specialized types of rock samples could be used. Obvious ones include (1) the iron- or manganese-oxide materials found in gossans, leached cappings, and vein fillings, and (2) fluid inclusions and geodes. Leakage halos may be present in the rocks cropping out above a mineral deposit that has not yet been exposed by erosion. In such an environment, the systematic sampling of any material suspected to be hydrothermally associated, such as iron- or manganese-stained fracture fillings or silica veinlets, could provide evidence of a concealed mineral deposit that would not be found by the sampling of only typical bedrock material. If veins are sampled, particular attention should be paid to the relationship, if any, between the vein orientation and the trace-metal content of the veins at each orientation, because veins of certain orientations may be of interest economically while those at other orientations may not (Rehrig and Heidrick, 1972).

Fluid inclusions are commonly thought to represent samples of trapped hydrothermal ore fluids; consequently, the concentrations of various elements in the material found in fluid inclusions in rocks may also prove valuable in exploring for copper deposits. In their study of a porphyry copper prospect in Puerto Rico, D. P. Cox and J. T. Nash (written commun., 1973) found that the fluid inclusions in quartz from rocks collected over or near the copper-rich exposures contain halite; similar inclusions from rocks collected outside the mineralized area do not contain halite. From a geochemical standpoint, then, a study of the trace-element content of fluid inclusions may provide a clue as to the location of copper deposits.

Geodes are another type of rock-sampling medium which might be useful for geochemical prospecting in the limited areas in which they occur. Because geodes crystallize from the outside to the center, the trace-element chemistry of the internal layers in a geode should reflect the chemistry of the environment surrounding the geode at the time the geode began to form. In this sense, geodes can be considered to be hand-specimen equivalents of fluid inclusions, and chemical analysis of geode interiors might be a useful means of studying some areas, especially those that have undergone deep weathering which might have leached more mobile elements such as copper from the surface rock and soil materials. The practical application of geode chemistry to geochemical exploration has not been demonstrated as yet, however.

SOILS

The use of soils in geochemical prospecting for copper has proved both popular and successful worldwide in many geochemical exploration programs. Soil sampling has been used mainly for detailed appraisals of limited areas rather than for regional reconnaissance programs. A review of the various routine applications of soils to prospecting is beyond the scope of this report; the reader is referred to comprehensive discussions such as those by Hawkes and Webb (1962, p. 202–226) and Bradshaw, Clews, and Walker (1970a, 1970b; 1971; 1972).

In most geochemical sampling techniques, it is important that persons collecting soil samples have an appreciation of the geology of the area being sampled and some idea of the characteristics of the soil being sampled. For example, it is important to know what soil horizon is being sampled and whether the soil is residual or transported.

A soil profile is commonly developed over bedrock except in most desert areas and in areas undergoing rapid erosion. It is important that orientation studies be made in any new area to determine information such as the best soil horizon for sampling as well as the best size of soil material to retain for analysis. Where present, the B horizon has most commonly been used for soil sampling because this horizon is normally enriched in metals relative to the A horizon. Under special conditions, the upper A horizon, which is rich in organic material, has also proved to be an effective sampling medium. Boyle and Dass (1967) reported that A-horizon soil samples from the Cobalt, Ontario, district contained higher concentrations of various elements including copper than did equivalent B-horizon samples. Their A-horizon samples also showed better anomaly contrast values. The authors attribute the higher metal values in the A horizon to biogeochemical enrichment processes. In another study, Curtin and others (1971) found that the ash of the forest humus layer (mull) from samples collected in the Empire district in Colorado was enriched in a number of base and precious metals as compared with concentrations of these metals in the underlying soils. The mull reflected known bedrock chemistry better than did the underlying soils, because the mull was derived from trees rooted in bedrock whereas the soils were derived mainly from transported glacial till.

The optimum grain size of soil material to be used for geochemical analysis should be determined for any new area being studied. The best size to use will depend on such factors as the original grain size of the minerals present, the degree to which these original grains have been eroded by weathering, and the anomaly contrast values obtained for each grain size. Hawkes and Webb (1962, p. 166) clearly demonstrated the effects of different grain sizes on concentrations for nine different elements.

In areas of transported cover, geochemical prospecting using soils has not been particularly useful. Hawkes and Webb (1962, p. 203) reported, however, that near-surface anomalies have been found over glacial till and alluvial deposits that were as much as 15 m (50 ft) thick. Apparently the metals causing the anomalies migrated to the surface either in the circulating ground water or through translocation from tree roots to leaves and then into the ground from the fallen leaves. Studies in humid areas (Curtin and others, 1971) and in arid areas (Chaffee and Hessin, 1971) have indicated that plants or plant materials are superior to soils as sampling media in areas containing soils derived from transported overburden.

Much better results have been obtained in soil sampling programs that utilized residual soil; however, the fact that the soil is residual does not assure that it will be a good sampling medium. Residual soil can form on top of transported material such as glacial till. In humid regions, deep residual soils are common, but they may have been so deeply leached by weathering that any copper minerals present would not be detected by analyzing samples for copper alone. Many of the circumpacific porphyry copper deposits, and some others as well, are enriched in gold as well as in copper. In the environment of deeply weathered residual soils in Puerto Rico, for example, the areal extent of gold-in-soil anomalies defined known porphyry copper deposits much more reliably than did the areal extent of copper-in-soil anomalies (Learned and Boissen, 1973).

A thorough evaluation of relatively immobile trace elements in soils and hydrothermally associated trace elements in resistate minerals remaining in leached soils should be helpful in locating copper deposits hidden under such soils. Studies of hydrothermal quartz grains from residual soils over several porphyry copper deposits in Puerto Rico, for example, revealed that halite-bearing fluid inclusions, which are known to be present only where copper minerals are present, are preserved in the residual soils and could be used to locate the deposits (D. P. Cox, written commun., 1973). The trace-element chemistry of these inclusions has not been determined as yet.

Silty frost boils proved to be the best type of soil-sampling material to use in the search for copper deposits in the Coppermine district of northern Canada where a perennial (continuous) permafrost zone exists. The boils acted as accumulators of fine inorganic soil material and were found to have a more uniform mineralogical composition than did the corresponding B-zone soils (Hornbrook and Allan, 1970).

Exploration geochemists conducting soil-sampling programs in arid areas should consider the possibility that eolian-transported silt- and clay-sized material may be intimately mixed with the residual soils of an area, thereby diluting metal concentrations in the soil. My investigations indicate that eolian dilution of metal concentrations should not be a problem in soil-sampling programs conducted in the southwestern United States; however, in desert areas of the Near East, wind-carried dust has been found to be an important dilutive factor which has to be considered (P. K. Theobald, oral commun., 1971).

Two other specialized types of soil-related material suitable for geochemical sampling are found in arid areas—caliche (calcrete) and desert varnish. Caliche is composed primarily of calcium carbonate that is deposited in warm arid climates as part of the soil-forming processes. Caliche often contains lithic impurities. In my experience, two types of caliche can be recognized; in sampling caliche it is important to distinguish between the two types. One type is commonly found interstratified in the sedimentary sequences of eroded gravels filling structural basins. These caliche layers represent old (now buried) and(or) modern soil horizons. Deposits of this type of caliche have never had any physical contact with bedrock and have no geochemical relationship to bedrock chemistry unless capillary action has moved mineral-rich ground water from areas of mineralized bedrock to the surface. Consequently, in most places, this first type of caliche is not suitable as a geochemical sampling medium. The second type of caliche is found at the present bedrock surface or along the bedrock-alluvium interface where bedrock is presently buried by alluvium. This second type is analogous to a residual soil horizon because it derives most of its trace-element concentrations from the underlying bedrock; consequently, this second type of caliche can be useful in geochemical prospecting. In his study of geochemical dispersion in the Twin Buttes, Ariz., porphyry copper district, Huff (1970) found anomalous amounts of copper in this second type of caliche in the vicinity of mineralized bedrock.

Desert varnish is an iron- and manganese-rich coating that forms on exposed surfaces of rocks in arid areas. It is probably the arid-environment equivalent of the iron and manganese staining found on stream sediments and float in the humid environment. In their study of desert varnish, Engel and Sharp (1958) found that it contained a variety of trace elements, including copper. Most of these elements were derived from the rock under the coating. In another study including areas containing mineralized rock, Lakin, Hunt, Davidson, and Oda (1963) found in many of the areas a rough correlation of enriched trace metals in varnish with known ore deposits containing these trace metals. No detailed study has as yet been made within a single district to establish positively whether or not desert varnish might be a useful geochemical sampling medium in copper exploration. Unfortunately, the occurrence of varnish within a given area may be restricted; consequently, it may not be possible to obtain samples at all desired locations.

SOIL GAS

Research in recent years has demonstrated that many volatile elements and compounds are associated with mineral deposits. Weathering processes and the action of micro-organisms tend to decompose the metallic minerals of a mineral deposit. Under ideal conditions, gaseous products, such as mercury, sulfur compounds, carbon dioxide, and others described later, can form at depth and migrate upwards to the atmosphere. If these gases are present in near-surface soils, they can be collected in an apparatus analogous to a funnel, which is placed on top of the soil at a given site (fig. 1) or collected in a probe placed in a hole drilled into the soil. Any gaseous products that are present in the soil can then either (1) be passed directly, without concentration, into some type of instrument that can measure the concentration of one or more gaseous components that have accumulated in the funnel or probe during a given time span; or (2) be trapped and concentrated at the funnel neck or within the probe by some chemical reaction. The trap can then be removed from the collection site and the gas analyzed for its components in a separate instrument.

Although it is a relatively new technique, the use of analyses of soil gas has proved feasible for the detection of various types of mineral deposits including those of copper. Where gases are present, the method offers a great potential for locating deposits covered with thick layers of glacial debris or other transported overburden. It might also be possible to use soil gases to detect deposits overlain by postmineralization-age volcanic flows if the flows have sufficient permeability.

In humid areas, water will be a complicating factor in soil-gas surveys because it will tend to inhibit

FIGURE 1.—Plastic hemisphere used in soil-gas sampling. The gases are collected either by using natural convection and a chemical trap attached to the top of the hemisphere, or by drawing the gases through a tube attached to the hemisphere and into an instrument designed to analyze gases. Scale is ≅30 cm long.

the upward migration of gases. In arid areas, however, where ground-water tables are either very deep or nonexistent, the use of soil gases to detect buried minerals should be an especially valuable technique. Mercury in air and in soil gas has received much attention as a possible pathfinder for base- and precious-metal deposits. In a review of volatile compounds as guides to ore, McCarthy (1972) noted that several workers have attempted unsuccessfully to find mercury anomalies in the air over porphyry copper deposits in the southwestern United States. Limited attempts to detect anomalous concentrations of mercury in soil gases over porphyry copper deposits have also proved unrewarding. The mercury concentrations may be too low to be detected with presently available instrumentation, or perhaps any anomalous concentrations of mercury have been dispersed well beyond the vicinity of a given deposit, and therefore were missed because sampling did not extend far enough beyond the deposit. In the final analysis, there simply may be no anomalous concentrations of mercury associated with porphyry-type copper deposits.

Gaseous products other than mercury vapor offer more promise in exploration for copper. Extensive soil-gas surveys have been conducted over copper-molybdenum deposits in the Soviet Union (Shipulin and others, 1973). These authors reported concentrations of O_2, N_2, H_2, CO_2, H_2S, SO_2, COS, and CH_4 in the soils overlying these deposits. Anomalous concentrations of the sulfur-containing gases were detected over areas of buried copper-molybdenum mineralization known to occur no closer than 30–60 m (100–200 ft) to the surface. These gases were not found in barren areas. In contrast, a buried barren pyrite body did not produce significant sulfur-gas anomalies. Several of the nonsulfur-containing gases were considered to be present because of atmospheric contamination, but their relation to the metal deposits, if any, was not described.

Rouse and Stevens (1971) detected anomalous concentrations of sulfur dioxide in soil gases collected from the Highland Valley porphyry copper district in British Columbia. Anomalous concentrations were found at the top of a glacial till layer that is as much as 600 m (200 ft) thick.

In their review of the use of volatile compounds in geochemical prospecting, Bristow and Jonasson (1972) indicated that the ratio of carbon dioxide to oxygen should be useful in soil-gas surveys. They noted that the gas-ratio method has been used successfully in the search for copper and other metals in various areas of the Soviet Union. Kravtsov and Fridman (1965) stated that oxidizing sulfides produce soil gases that contain less oxygen and more carbon dioxide and hydrogen sulfide than do the soil gases found in normal soils. These authors found increased amounts of hydrogen sulfide and sulfur dioxide in soils near chalcopyrite deposits.

Chitayeva, Miller, Grosse, and Christyakova (1971) described the presence of iodine in the supergene zone of the Gay chalcopyrite deposit in the Soviet Union. They found the iodine anomalies directly above the copper ore body and suggested that iodine should be a good pathfinder element to use in overburden surveys. Undoubtedly other soil gases will be found associated with copper deposits. Various authors have described the detection of different volatile compounds from mineral deposits other than copper deposits. For example, Ovchinnikov, Sokolov, Fridman, and Yanitskii (1973) detected helium, neon, argon, hydrogen, carbon dioxide, nitrogen, sulfur dioxide, hydrogen sulfide, methane, and the halogen gases in rock, soil-gas, and ground-water samples. In addition to many of the gases mentioned above, Kravtsov and Fridman (1965) found complex hydrocarbon gases ranging from methane to hexane associated with ore deposits.

TRANSPORTED MATERIALS

The use of transported material as a geochemical sampling medium presents especially challenging problems. Because transported materials have often migrated great distances from their original source rocks, the geochemist using these media must have a knowledge of both the local and regional geological and geochemical environments in order to interpret his geochemical data properly. In spite of the obvious handicaps, transported material has been used successfully in many different exploration programs. Three types of transported material are discussed: these are glacial debris, stream sediments, and lake sediments.

GLACIAL DEBRIS

The use of glacial debris as a geochemical sampling medium has found wide application in reconnaissance surveys, especially in Canada, Scandinavia, and the Soviet Union. It is important that persons conducting and interpreting geochemical sampling programs involving glacial debris have a thorough understanding of the history, nature, and mode of formation of the glacial deposits present in the areas they examine. A sampler must, for example, be able to distinguish the origin of fine sediment that might be from till fines, former lake sediments, or glaciofluvial material. Various studies have indicated that basal till material is almost analogous to residual soil; lake-sediment deposits and glaciofluvial deposits, on the other hand, may be formed from material that has been transported long distances.

The distance that till fragments have been transported from their source is generally determined by recognizing rock fragments in the till that are unique to some known source rock upglacier. Although till fragments have been found as much as 1,100 km (700 mi) from their source, probably more than 90 percent of all such material has travelled only about 1½ km (1 mi) (Chamberlain, 1883). In Sweden, about 70 percent of all till is thought to be locally derived (Lundqvist, 1967).

The successful use of till samples in reconnaissance surveys for copper deposits has been widely documented in the literature (Hawkes and Webb, 1962, p. 186–190; Bradshaw, Clews, and Walker, 1971; Garrett, 1971) and will not be described in detail here.

In general, till is a very heterogenous type of material that ranges in size from clay-sized particles to large boulders. Different sizes of material have been used in different types of surveys. Trains composed of large rock fragments or boulders (float) in till have been used successfully in geochemical prospecting for copper and other metals as well as in geological mapping (Dreimanis, 1958; Lee, 1971). From a purely geochemical standpoint, however, most sampling schemes have utilized fine material collected at the base of the till.

Many metallic elements, including copper, are preferentially enriched in the fine fraction of till sediments. Shilts (1971) stressed the importance of relating the amount of clay-size material in a sample to the relative concentrations of the elements under study. To properly evaluate till anomalies, Shilts suggested removing the clay-sized material from the silt-sized material before analysis of the sample. He also suggested using a heavy-mineral concentrate from the till sample as an alternate type of sample medium.

Esker gravels, a glaciofluvial type of deposit, have been used successfully as a sample medium in Canada (Lee, 1965; 1971). In his study of the distance of transport of material in esker gravels, Lee (1965) found that rock fragments had been carried an average distance of 5–13 km (3–8 mi) from known bedrock sources. Sampling of esker gravels is obviously limited by the areal extent of esker deposits; however, eskers are known that are several kilometres wide and as much as several hundred kilometres long, so that relatively large areas can be prospected using esker material. The technique should be especially useful where an esker crosses the structural and(or) stratigraphic grain of a region.

STREAM SEDIMENTS

The most universally accepted and most successful of all geochemical-prospecting techniques is stream-sediment sampling. Stream sediments probably reflect more accurately the upstream geology and chemistry of a large area than do any of the other types of sample media. As a consequence, the technique is extremely useful for rapid regional-reconnaissance geochemical surveys. The method is also very valuable for most detailed work in drainage basins found during reconnaissance work to contain anomalous metal concentrations. The technique has had wide application in the search for copper in many different geologic and climatic environments. Many examples are described in the geochemical literature.

In stream-sediment surveys in which copper is the element sought, the sampling environment must be carefully considered. For example, in humid climates where acid soil conditions and thorough chemical decomposition of rocks generally prevail, stream sediments should be analyzed for cold-extractable copper rather than for total copper. Stream sediments have been analyzed for cold-extractable copper as part of surveys performed both in tropical humid areas such as the Philippine Islands (Govett and Hale, 1967), and in temperate humid areas such as Maine (Post and Hite, 1964).

Less chemical breakdown of rocks takes place in arid areas than in warm humid areas; consequently, copper may be dispersed in arid areas more by mechanical means than by chemical means (fig. 2). Also, in an arid environment, metal-rich ground water does not normally come in contact with stream sediments. Because of these facts, a total (hot-acid-extractable) analysis for copper has been used in many geochemical studies conducted in arid areas (Awald, 1971; Coolbaugh, 1971). It should be emphasized, however, that there is not as yet enough information relating the type of copper analysis to the type of environment. Orientation studies should be run in any new area to determine which type of copper analysis gives the best anomaly contrast for that area.

A major concern in stream-sediment surveys has been the interpretation of the effects, if any, of secondary hydrous iron-manganese scavenging on the concentrations of other metals in the samples. Jenne (1968) made a comprehensive laboratory study and literature review of the role of hydrous iron and manganese oxides in scavenging (coprecipitating) heavy metals, including copper. He concluded that these two oxides (especially that of manganese) are the most important controls on the fixation of copper, cobalt, nickel, and zinc in soils and stream sediments. Chaffee, Botbol, and Hamilton (1972) applied a factor-analysis program to a data set containing analyses of more than 6,000 stream-sediment samples collected throughout central Maine. In contrast to Jenne's conclusions, the factor analysis clearly demonstrated that, at all factoring levels, the copper concentrations in the samples (both cold-extractable and spectrographic copper) were not related to either the iron or manganese concentra-

FIGURE 2.—Typical desert wash used in stream-sediment sampling in semiarid southern Arizona. Note the poor sorting of the active sediment.

tions. Data from this study seemingly indicate that copper is not scavenged by secondary hydrous iron and manganese oxides. Insofar as copper is concerned, the relation of copper enrichment to the content of iron-manganese oxides in stream sediments is not yet completely defined. The study by Chaffee, Botbol, and Hamilton (1972) indicated that iron and manganese oxides do coprecipitate and concentrate such elements as cobalt, zinc, lead, and molybdenum. If any of these four elements is used as a pathfinder in the search for copper deposits, then the effect of secondary iron and manganese oxides should be considered in data interpretation.

The U.S. Geological Survey is currently making a study of the source of the secondary metals associated with stream sediments. Present information suggests that where metal-rich interstitial ground water flows into a stream from bank soil, there are abrupt changes in the physical and chemical environment. These changes cause the metals to precipitate in the stream, either as grain coatings or as small nodules, before they are transported very far downstream. Most of the cold-extractable metals found in stream sediments are thought to have been derived from these interstitial ground waters, even though stream waters usually constitute a much larger proportion of the total water volume at a given stream locality (G. A. Nowlan, oral commun., 1973).

As was mentioned in the section on soil surveys, the optimum size of material, in this case stream-sediment material, used for analysis should be determined in any new area. Most, but not all, elements are concentrated in the sediment fines; however, the best grain size to retain for analysis should be the one that provides the best anomaly contrast. Hawkes and Webb (1962, p. 256–258) have given an excellent discussion of this problem.

Most stream-sediment surveys have used the fine-grained (−80 mesh) fraction for analysis; however, Fisher (1970) reported that in some areas of Australia, stream-sediment material as coarse as a −20 to +40 mesh fraction gave better results than did standard −80 mesh fractions. Different climatic, geologic, and terrain conditions were found to influence the metal content of different size fractions.

The importance of selecting the proper size of sample material to use in a stream-sediment survey was also emphasized by Erickson, Marranzino, Oda, and Janes (1966). Their study was conducted in an arid area of eastern Nevada not known to contain any significant metal occurrences. The authors concluded that the most successful method for finding new deposits in that terrain was analysis for base metals and mercury of float cobbles and pebbles collected in the major stream channels. Chemical data from the −50 mesh fraction of stream-sediment samples failed to reveal any anomalous metal concentrations except in those samples collected from streambeds draining a previously known but abandoned small mining district.

Several types of concentrates, including magnetic and nonmagnetic heavy-mineral concentrates and grain-coating concentrates, can be made from standard stream-sediment samples. Analyses of these specialized samples are sometimes more useful in defining geochemical anomalies in stream channels than are the analyses of the original stream-sediment samples from which these specialized samples are derived. Griffitts and Alminas (1968) collected stream-sedimnt samples in an arid area of southern New Mexico and made heavy-mineral concentrates from these samples. They found that their analyses of the nonmagnetic heavy-mineral concentrates provided more information for locating mineralized areas than did the analyses of the corresponding samples of standard −80 mesh stream sediment. Huff (1971) experimented with different subsamples as possible guides to a known porphyry-copper district in southern Arizona. He sampled sediments from streams draining the copper deposits present and found that the copper concentrations in (1) ultrasonic concentrates of sediment grain coatings, (2) the nonmagnetic heavy-mineral fraction, and (3) hydrothermally-altered stream pebbles all located the known deposits as well as or better than did the standard −80 mesh fraction of the stream-sediment sample.

Heavy-mineral concentrates from old placer districts may be useful in the search for copper deposits. In a study of placer minerals in Taiwan, Tan and Yu (1968) found that placer gold was present in the sediment from streams draining known copper-gold deposits. The worldwide association of gold with many copper deposits suggests that gold in stream-sediment concentrates should be a valuable pathfinder element in the search for copper deposits.

The concentrations of camouflaged trace elements in heavy-mineral fractions of stream sedimnts can also be used in geochemical exploration for copper deposits. Tan and Yu (1968) detected anomalous concentrations of copper in pyrite concentrates collected from streams draining areas of known copper deposits in Taiwan. In another study, Bell and Hornig (1970) determined that iron-oxide pseudomorphs after pyrite may be a useful geochemical-sampling medium in the search for sulfide deposits in deeply weathered regions. These authors found iron-oxide pseudomorphs to be a common constituent in stream-sediment samples as well as in soil and saprolite samples that they collected in South Carolina. These pseudomorphs contained appreciable amounts of many trace elements. The authors suggested that the regional variation in trace-element content of the pseudomorphs may be a guide to areas of sulfide mineralization.

In a study of alluvial magnetites from streams in central Ecuador, de Grys (1970) found that the copper and zinc concentrations in the magnetites were useful in defining various base-metal deposits. She noted that it was important to determine whether the magnetite was fresh or weathered. In fresh magnetite, all the trace elements were considered to be primary; altered magnetite might contain secondary hydrous iron-oxide coatings that could coprecipitate other metals.

As noted in the section on rocks, my experience suggests that caution should be exercised in interpreting trace-element data from magnetites and possibly from other heavy minerals. In complex geologic terranes, different geologic formations may contain magnetites or other heavy minerals having different ages and geneses. These formations will, therefore, probably have different suites of trace elements. A knowledge of bedrock geology is thus essential for the proper interpretation of any alluvial heavy-mineral data.

Because of the large amount of information that can be generated from regional stream-sediment sampling programs, computer analysis of the analytical and other data is becoming more and more important for evaluating the data. Many computer programs are now available to treat large data sets. Some of these methods are discussed later in this report.

LAKE SEDIMENTS

In recent years, the collecting and analysis of lake sediments has been another useful geochemical-prospecting technique, especially for regional reconnaissance surveys. This method, which is especially applicable to remote areas where sampling can be done from pontoon-equipped helicopters or small fixed-wing aircraft, has been used successfully in regional-reconnaissance copper exploration programs in Canada. Field studies (Allan, 1971; Allan and Crook, 1972; and Allan and others, 1972, 1973) have demonstrated that standardized samples can be taken from lake sediments and that the chemical analyses from these samples can define areas enriched in copper as well as can those from stream-sediment samples. Best results were obtained from samples of sediment collected 5 to 15 cm (2 to 6 in.) below the lake-bottom surface at depths of about 90 to 240 cm (3 to 8 ft) below the lake-water level. Although clay-sized material made the best sample, the use of clay- and silt-sized material together (about 50 micron and smaller-sized material) proved to be a useful sample that could be quickly obtained and prepared for analysis.

Factors such as Eh, pH, organic content, and secondary iron- and manganese-oxide content that can affect stream-sediment sample data can also affect lake-sediment sample data. Furthermore, it is important to recognize that the lake-sediment chemistry reflects that of the sediment source area and not that of the bedrock below the lake.

WATER AND RELATED MATERIALS

Marine and fresh water, as well as ice and snow, represent potential geochemical sampling media, but they have not been widely used because a great many parameters can influence the chemical data obtained and because only extrême low metal concentrations are normally found. With the development of more sensitive and accurate analytical techniques and new computer programs, these media are becoming more useful in geochemical studies.

WATER

Hydrogeochemical prospecting techniques have been reviewed in detail by Hawkes and Webb (1962, p. 227–246) and by Boyle and others (1971). Most hydrogeochemical surveys have been conducted using lake water as the sampling medium; however, waters from streams, springs, seeps, wells, and the sea have also been used.

Water has not been a popular sampling medium because a great many physical and chemical factors must be considered in evaluating water analyses. Some of these factors are Eh, pH, the overall chemistry of the environment sampled, the distance from the source of metals to the sample site, the time of year, the duration, type, and annual rate of precipitation, the ambient temperature, the size and rate of flow or circulation of the water body, and the effect of organic matter. The form in which metals occur in water has also caused difficulties in data interpretation. Metallic elements such as copper can occur in natural water in many different forms, including free ions or undissociated molecules, ions adsorbed on suspended matter, and water-soluble metallo-organic complexes. Metals may also be found in organic gels, in waterborne micro-organisms, and in suspended matter such as colloids or finely divided inorganic sediment.

Kleinkopf (1960) sampled lake waters in Maine and demonstrated that clusters of lakes there contained anomalous amounts of copper, molybdenum, and other metals. In some areas he found an association between the anomalous concentrations of metals in the water samples and the known geology and mineralized rock bodies.

In a more recent study of lake waters conducted specifically for copper exploration, Allan (1971) and Allan, Lynch, and Lund (1972) analyzed lake-water and lake-sediment samples collected in a large region around the Coppermine district in Canada. Although the distribution of copper in lake-sediment samples gave the best indication of areas known to be enriched in copper, the distribution of copper in lake-water samples also successfully delineated the areas of highest copper concentration in the region. Seasonal and intra-lake chemical variations were not found to be serious problems for interpretation.

Boyle and others (1966) conducted a regional geochemical survey in New Brunswick, Canada, in which they collected samples from stream waters and stream sediments. Stream-water samples, even near known base-metal deposits, had very low concentrations of copper. Analyses of zinc and cold-extractable heavy metals in the water gave much better results; however, data for all elements from the stream-sediment samples provided better information than did the comparable water data.

In another study, Boyle and others (1971) showed that dispersion trains of metals in stream waters are usually more restricted than those in stream sediments. Consequently, these authors recommended using stream-sediment samples for regional reconnaissance surveys, and stream-water samples for detailed surveys. They recommended that all water samples be collected as near as possible to the headwaters of stream tributaries.

In some regions of the world the ground is frozen all year long (continuous permafrost) or at least part of the year (discontinuous permafrost). Until recently, the presence of continuous permafrost has suggested to most geochemists that metals would have little chance to migrate upwards to the surface; however, thawed ground is now known to exist in areas of continuous permafrost under and around streams and large bodies of water such as lakes (Allan and Hornbrook, 1971). Shvartsev (1972a, 1972b) successfully used samples of spring waters that have circulated through permafrost zones to locate buried base-metal deposits in the Soviet Union.

Water from seeps and cold springs, and the precipitates that form around them, have been found useful in geochemical surveys (Boyle and others, 1971; Shvartsev, 1972a, 1972b; Mehrtens, Tooms, and Troup, 1973). Water from hot springs, on the other hand, has not been successfully used as yet to locate copper deposits. Many—perhaps most—hot springs have no obvious relationship to potential copper deposits; however, White (1967) described the chemistry of some hot springs and hot-spring deposits that are associated with base-metal deposits in Japan and the United States. Weissberg (1969) made a similar study of some thermal areas in New Zealand. Both authors noted that base metals are not normally present in significant amounts in the waters issuing at the ground surface, but were found at depth in samples of drill core. The waters issuing at the surface commonly contained such ions as Ca^{+2}, Na^{+}, Mg^{+2}, Li^{+}, F^{-}, Cl^{-}, Br^{-}, $SO_4{}^{-2}$, and $HCO_3{}^{-}$ and the discharge precipitates contained such metals as Au, Ag, As, Sb, Hg, Tl, Fe, and Mn. Apparently, most of the heavy-metal ions, including copper, are precipitated below the surface; thus, geochemical exploration programs using samples of hot-spring waters will probably have to rely on some combination of pathfinder elements as guides to buried copper deposits.

The study of ground-water geochemistry can be valuable in geochemical prospecting. For most exploration purposes, wells, drill holes, and possibly old shafts or quarries are the only feasible places for sampling subsurface waters. Wells are especially useful sources in arid areas where there is very little surface water.

In arid areas, the ground water is normally alkaline except perhaps near oxidizing sulfides. In the alkaline environment, very few elements are mobile; however, in the absence of high concentrations of such ions as manganese, iron, carbonate, and sulfate, the metals chromium, molybdenum, and tungsten are fairly mobile. Copper is generally not very mobile at high pH levels. Huff (1970) was able to detect the buried copper-molybdenum deposits of the Pima district in Arizona by measuring the molybdenum concentrations in well-water samples. He found a molybdenum anomaly that extended as much as 13 km (8 mi) downslope from the known deposits; copper was not present in anomalous concentrations in these samples.

Well waters have been sampled for molybdenum throughout much of the southwestern United States by various private companies; however, little information has been made public. Anomalous molybdenum concentrations in well water are known to exist downslope from known copper-molybdenum deposits, but to date no new deposits have been found using well water as the sampling medium. No information about the content of tungsten or chromium in well waters is available.

The mineral potential of the world's oceans and ocean bottoms is gradually being recognized. The presence of copper in deep-sea manganese nodules, in manganese-rich encrustations on rock- and sediment-grain surfaces, and in bottom deposits such as those of the Red Sea, is already well known. At present we have little detailed knowledge of the movement of trace elements in ocean waters and how trace-element dispersions in marine waters might be used in geochemical prospecting for nearshore or deep-sea mineral deposits. Additional fundamental chemical and physical data concerning the oceans are needed before geochemists can begin to apply geochemical prospecting methods successfully to samples of ocean waters and bottom materials. In some deep-sea areas, the regional trends in the chemistry of near-bottom waters or of slowly upwelling waters may be useful in locating any deep-sea copper deposits that are not buried under thick layers of barren sediment. In many localities, submarine springs are known to be present. Analyses of samples of this type of spring water might be useful in determining the presence of anomalous concentrations of metals in the source aquifer.

In the future, deep-sea metal-rich bottom-sediment deposits, such as those found in the Red Sea and elsewhere, may well be an economic mineral resource. Holmes and Tooms (1973) made a reconnaissance geochemical survey of part of the Red Sea area. They collected samples of surface waters as well as samples of bottom sediment and near-bottom water from depths of about 2,000 m (6,500 ft). The dissolved metal species in the near-bottom water samples and the particulate matter in these samples were analyzed separately. Significant anomalies were found in all the sample media except those from the surface waters. This study suggested that reconnaissance geochemical surveys should be successful in locating deep-sea metal-rich bottom-sediment deposits as well as deep-sea brines that contain high concentrations of various metals.

Material suspended in fresh water has recently been considered as a possible geochemical sampling medium. Perhac and Whelan (1972) compared the metal content of stream water, of bottom sediment, and of the suspended colloidal and coarser particulates in the water. The colloidal material was found to be greatly enriched in metals, including copper, as compared with the other types of samples. Because the separation of colloidal samples for analysis requires expensive equipment and an inordinate amount of time, the method is not very practical at present.

Timperley, Jonasson, and Allan (1973) found that most lakes in certain parts of Canada contained organic gels that may occur as much as 13 m (30 ft) above the inorganic sediment of lake bottoms. The gels are thought to include (1) organic precipitates of colloidal origin, (2) residual organic matter derived from decaying vegetation, (3) pollen, and (4) finely divided inorganic mineral matter. Preliminary data indicated that the gels contained concentrations of various elements, including copper, and that the trace-element concentrations of the gels can be related to the local geology. The use of organic gels from lakes as a regional geochemical sampling medium seems promising.

Gels also are found along shorelines where freshwater rivers discharge into bodies of saltwater (W. C. Overstreet, written commun., 1973). The extent of such gels along shorelines is not known, but if these gels are commonplace, then systematic sampling of them could be another effective reconnaissance geochemical exploration technique.

Gases are commonly dissolved in all types of natural waters. Analysis of radon gas in lake and stream waters has been used in Canada as a reconnaissance hydrogeochemical exploration method in the search for uranium deposits (Dyck and others, 1971); however, the analysis of gases in waters has not as yet been applied to copper exploration.

ICE

The use of samples of ice in a geochemical sampling survey is obviously quite limited but may be feasible. Shvartsev (1972a) has attempted to use naleds as a geochemical sampling medium. Naleds are ice sheets that form during the cold season in areas of discontinuous permafrost. They form where subsurface water is forced to the surface and flows out over the surface and is frozen. Shvartsev noted that there has not been sufficient work done on naled geochemistry to determine whether the sampling of naleds will be a useful technique for locating mineral deposits in cold regions.

SNOW

Traces of Cu, Hg, Zn, Pb, Ag, Mn, Cd, As, and Ni have been detected in snow samples collected from sites overlying several types of buried mineral deposits in Canada (Jonasson and Allan, 1973). Their study revealed that these metals were derived at the time of the first snowfalls from the weathered mineralized rocks below the soil horizons and not from particulate matter present in the air above these rocks. These authors concluded that snow may be a useful sampling medium but that its use is limited to detailed prospecting in areas of known mineral potential.

VEGETATION

Vegetation can be used both in geobotanical and biogeochemical prospecting. Geobotanical prospecting involves noting and mapping (1) the presence and abundance of, or (2) the absence of, a plant species or plant community with relation to soil and rock enriched in a given element such as copper. Geobotanical prospecting may also involve noting and mapping the presence of morphological and(or) mutational anomalies in plants. In contrast, biogeochemical prospecting involves analyzing plant materials for their trace-metal content in order to locate areas of high metal concentrations.

GEOBOTANICAL TECHNIQUES

Geobotanical prospecting has been discussed in detail by Brooks (1972). Where this technique is successful, it is a rapid and inexpensive prospecting method. Brooks (1972) noted that plant communities indicative of soils enriched in certain elements or indicative of certain rock types have been recognized for more than a century; however, no plant communities are known that uniquely define copper-enriched soils. Several individual plant species, on the other hand, have been found to be associated with copper-rich soils in different parts of the world. Cannon (1971) listed 30 species of plants that have been used in various localities as indicators of copper. She noted that geobotanical prospecting has been especially successful in the search for copper in Australia, Katanga, China, and the Soviet Union. Cannon (1960) also stated that most copper-indicator plants belong to one of three plant groups; (1) the Caryophyllaceae, or pink family; (2) the Labiatae, or mint family; (3) the mosses.

My geobotanical studies in the porphyry copper region of the southwestern United States as well as those by Lovering, Huff, and Almond (1950), Warren, Delavault, and Irish (1951), and Cannon (1960) indicate that abundant populations of the California poppy (*Eschscholtzia mexicana*) grow in close association with copper-rich soils near many porphyry deposits. Unfortunately, the poppies are not found growing over all cupriferous soils of the region nor are all wild poppy populations associated with cupriferous soils. Evidently the conditions promoting vigorous poppy populations involve more than the mere presence of high copper concentrations in the soil. During the period of flowering, localities containing the poppy are easily recognized both from the ground and from the air at low altitudes. Areas containing the poppy certainly warrant close examination.

Despite studies by many workers, no other important copper-indicator plant species has been identified for the porphyry copper region of the United States. However, Cannon (1971) has described some plant species that are commonly associated with sulfur- or sulfate-rich soils; I have seen some of these species growing in soils formed from rocks containing oxidizing sulfides. Unfortunately, these species do not differentiate between biogenic-sedimentary sulfide and sulfate concentrations, and hydrothermally-introduced sulfide and sulfate concentrations.

A high content of copper in soils can cause morphologic or mutational changes in certain plant species or can cause the complete absence of vegetation. Cannon (1960, 1971) and Brooks (1972) have described areas in widely separated parts of the world in which copper-rich soils caused such effects.

BIOGEOCHEMICAL TECHNIQUES

Chemical analyses of plants or plant parts can be used as a geochemical-prospecting technique when it can be shown that the chemical content of the vegetation sampled has some predictable relationship to the chemical content of the nutrient soil or bedrock, or at least to the ground water moving through the soil or bedrock. Only some brief comments related to copper will be given here; for more details the reader is referred to Brooks (1972).

Biogeochemical prospecting requires specialized knowledge and equipment beyond that needed, for example, for rock or soil sampling, and these requirements generally determine where the method can be used most effectively. The primary advantage of biogeochemical sampling over the methods of surficial sampling is predicated on the fact that many plants are deep rooted. Chemical elements absorbed by a deep well-developed root system are commonly translocated to the leaves and stems of the plant. The leaves and(or) stems can then be collected for analysis. Roots growing to depths of as much as 66 m (200 ft) have been documented (Brooks, 1972, p. 107). With these facts in mind, it can be seen that biogeochemical sampling should be a better technique than soil or rock sampling in regions of extensive but relatively thin postmineralization-age overburden. This overburden may include glacial deposits, talus, or landslide deposits, desert pediment gravels, or even fairly recent organic accumulations such as peat or deep humus soil layers found in areas of dense vegetation.

The mechanisms by which plants translocate and concentrate trace elements are not well understood. Many physical and chemical parameters such as soil Eh and pH, annual precipitation rate, mean annual temperature, aspect, soil type and texture, antagonistic effects of elements present, and physiology of each plant species, control the ultimate locations and concentrations of each element. As a result, sampling and analyses of plant material should be done on a consistent basis to minimize the effects of these parameters.

Probably the most common use of the technique of biogeochemical prospecting has been in areas covered with glacial deposits in Canada, Scandinavia, and the Soviet Union. Wolfe (1971) concluded that this method can be an effective technique under optimum conditions, but that if impermeable layers of clay and silt are present in the glacial substrate, such layers will prevent the upward migration of metals from mineralized bedrock below the layers, and no anomalous concentrations of metals will be present in plants, even in those growing directly over ore. This author also stated that, in contrast to other regions, most trees of the Canadian Shield probably do not have root systems that extend below 6–16 m (20–50 ft). This maximum depth of rooting reflects primarily the presence of shallow water tables and (or) impermeable clay or silt lenses. The maximum rooting depth of plants may also be controlled by frozen layers in the zone of discontinuous permafrost. Biogeochemical prospecting in glaciated regions will therefore be most successful in areas covered only by thin glacial debris composed mainly of unfrozen, coarse, porous sediment.

In a review of studies of vegetation conducted in the Soviet Union, Nesvetaylova (1961) described one case in which the iron content of the ash of birch leaves effectively outlined an area of copper-rich ore deposits. In Canada, Warren and his colleagues (Warren and Howatson, 1947; Warren, Delavault, and Irish, 1949) collected samples of a variety of tree species and several different tree parts. The chemical data from these plant samples provided information that helped to delineate some copper-rich localities in western Canada. In these studies Warren and his co-workers emphasized the use of copper-zinc ratios from the plant ash analyses as an aid in evaluating their data.

Peat, another type of biogeochemical sampling medium, is commonly found in humid regions. Samples of peat have been used successfully in both regional and local surveys in the search for copper deposits in many parts of the world. In Finland, Salmi (1967) discovered that anomalous concentrations of trace elements in peat ash could be used to locate copper and other types of mineral deposits buried under shallow layers of peat and glacial till. In Sweden, Brundin and Nairis (1972) found that the analytical data for copper from peat samples were superior to corresponding data from water and stream-sediment samples for delineating known mineral deposits. In the Soviet Union, anomalous concentrations of copper were found in samples of peat collected 300 to 600 m (985 to 1,970 ft) down drainage from a known copper deposit. (Al'bov and Kostarev, 1968).

Gleeson and Coope (1967) successfully located buried base-metal deposits in Canada by using peat as a sampling medium. They noted that the metals found in peat were probably derived from ground water circulating through the peat and that the metal content of the peat samples is related to the degree of humification of the peat and the pH of the associated waters.

Biogeochemical prospecting has also been applied to the search for copper in an arid environment, particularly in the porphyry copper province of the southwestern United States. In desert regions there is an important dichotomy of plant types caused principally by the depth of the permanent ground-water table in a given area. Riparian plant species—those that grow almost exclusively in and along intermittent or permanent stream channels—are mostly phreatophytes; that is, species that have extensive root systems that reach to the permanent ground-water table (fig. 3). Nonriparian plant species, on the other hand, grow almost anywhere including in intermittent stream channels and are mostly xerophytes, that is, species that have shallow root systems and that obtain their water from intermittent rainfall and not from the permanent ground-water table. The sampling of riparian species is somewhat analogous to collecting stream-sediment samples, and the sampling of nonriparian species is analogous to collecting soil or rock samples.

Because of the generally poor development of soils in arid regions, most residual soil horizons are fairly thin; consequently, as long as any residual

FIGURE 3.—Mesquite (*Prosopis* sp.) roots are exposed in a wash near Tucson, Ariz. The deep, well-developed root system is typical of this phreatophyte and makes this species especially useful as a biogeochemical sampling medium in this semiarid region. From Huff (1970, fig. 6).

soil is available, there is rarely any reason to sample nonriparian plant species. In areas containing fairly thin layers of transported overburden, however, nonriparian species may give a better indication of buried mineral deposits than can the soils derived from the transported overburden. Plots of concentrations of copper, zinc, and molybdenum in plant ash from samples of plants growing in thin layers of transported pediment gravel deposits overlying the Vekol porphyry copper deposit in central Arizona showed limited but more widespread anomalies than did plots of the corresponding soil data (Chaffee and Hessin, 1971; and Chaffee, unpub. data).

Work by Huff (1970) and Brown (1970) and my studies clearly indicate that where phreatophytes are available they are an effective sampling medium for copper exploration. Mesquite (*Prosopis juliflora*) has been the most widely used phreatophyte in biogeochemical surveys in the arid regions of the western United States. Use of samples of this species has been successful partly because mesquite grows in warm areas over a wide region extending from southeastern California to southern Kansas and partly because its root system can penetrate to great depths. A live root tentatively identified as being from a mesquite plant was collected from an open-pit mine in southern Arizona at a depth of about 53 m (175 ft) (Phillips, 1963). This depth undoubtedly represents an extreme, but roots to depths of about 15 m (50 ft) are probably common.

In the Pima district in Arizona, Huff (1970) detected anomalous concentrations of molybdenum in the ash of mesquite stems collected as much as 13 km (8 mi) away from any outcrop of mineralized bedrock. Brown (1970) also found anomalous concentrations of copper in the stem ash of samples of mesquite collected over the Kalamazoo porphyry copper deposit near San Manuel, Ariz. This anomaly extended well beyond the exposed parts of the deposit into transported colluvial gravels. I have also been successful in locating partially buried porphyry copper deposits in Arizona by using analyses of copper, zinc, and molybdenum in the ash of leaves and stems of mesquite. Analyses of the ash of other species, including those of catclaw (*Acacia constricta*), blue paloverde (*Cercidum floridum*), and a nonphreatophytic species, ironwood (*Olneya tesota*), have proved nearly as effective. Plants of these species have been found to contain anomalous concentrations of copper, zinc, and(or) molybdenum at sites at least 3 km (about 2 mi) downstream from any mineralized outcrop. Clearly, biogeochemical prospecting is an effective regional reconnaissance technique in the search for copper in an arid environment.

MICRO-ORGANISMS

Micro-organisms (mostly bacteria and algae) may be useful in geochemical prospecting. The role of micro-organisms in geological processes has been reviewed in detail by Kuznetsov, Ivanov, and Lyalikova (1963). Essentially all the data in the literature deal with the relationship of micro-organisms to fossil-fuel, iron, or sulfur-sulfate deposits, or to the use of bacteria in the leaching of low-grade mine wastes for the recovery of base and ferrous metals.

Apparently, very little research has been done on the subject of the use of micro-organisms in the exploration for ore deposits. The only practical application of micro-organisms in the search for ore deposits was done in the Soviet Union (Kuznetsov, Ivanov, and Lyalikova, 1963). This study showed that thiobacteria were present in material of an undescribed nature overlying a molybdenum ore deposit. Circulating waters above the deposit were distinguished from the regional ground water by the concentrations of certain types of bacteria.

In an analogy to vegetation surveys, micro-organisms could be used in geochemical prospecting in two ways. First, the presence or absence of, or the abundance of, certain types of micro-organisms may indicate the presence or absence of certain chemical species, such as sulfur or sulfate. Second, the organisms themselves can be collected and analyzed for their chemical content of any given element.

It should be feasible to study soil micro-organisms by making cultures of them in various culture media. If cultures can be found that will produce organism growth or death only in the presence of anomalous concentrations of copper, for example, then it should be possible to collect small amounts of soil over areas of interest and to run cultures to determine the content of copper or of some other element in those soils. This procedure has not been tested as yet; if successful, it might be more rapid than routine chemical analysis of the soils (H. W. Lakin, oral commun., 1973).

Plankton are known to be concentrators of metals (Warren, Delavault, Fletcher, and Peterson, 1971). Sampling of plankton growing at the mouths of rivers might be a good reconnaissance geochemical prospecting method to use along marine or large-lake shorelines. Samples of algae collected from the mouths of rivers in Puerto Rico have been found to contain anomalous amounts of copper. Whether the anomalous samples are from the mouths of rivers draining areas containing porphyry-copper-type minerals has not been established (R. E. Learned, oral commun., 1973).

ANIMALS

Studies in recent years have shown that animals can be used in two different ways in geochemical exploration. First, dogs can be trained to scent sulfide minerals. Second, animals in general tend to accumulate trace elements in their tissues and waste products; thus, these materials can be used as a type of biogeochemical sample.

In the last 10 years, dogs have been used increasingly as an aid to geochemical prospecting in Canada and in Fennoscandia (Brock, 1972). Dogs have olfactory senses far superior to those of man; consequently, they can be trained to scent sulfide minerals. The widest application of dogs to geochemical prospecting has been in locating sulfides in glacial moraines (Nilsson, 1971). In field trials, dogs have been able to find sulfide minerals where no human could have found them by visual inspection alone. The dogs have found sulfide minerals buried under 30 cm (1 ft) of overburden (Stirling, 1972). They have also found pieces of sulfide float in the fines of stream sediments (Brock, 1972). In Finland, a dog found boulders containing pyrite and chalcopyrite that were later found to be associated with a "copper ore body of economic significance" (Stirling, 1972).

Another animal that has been studied as a potential aid to geochemical prospecting is the termite. Termites are found throughout the tropical and subtropical regions of the world and in temperate regions to about lat 45° N. and S. All told, these regions constitute about two-thirds of the Earth's land surface (Lee and Wood, 1971). Many termite species build mounds above ground, most species construct extensive subterranean galleries. Although galleries have been reported to extend to depths of 70 m (230 ft) (Yakushev, V. M., in Lee and Wood, 1971, p. 53), most termite galleries are at much shallower depths. Watson (1972) observed termite galleries at least 23 m (about 75 ft) deep in mine workings. He believed that termites constructed these deep galleries in their search for the ground-water table. These observations suggest that the material present in termite mounds might represent deeply buried material and that these mounds could be used as a sampling medium for geochemical prospecting in overburden in termite-infested regions. However, in his studies of the Kalahari sand of Africa, Watson (1970, 1972) found that most of the material from termite mounds was derived from depths of less than 3 m (10 ft), despite the fact that the termite galleries extended to much greater depths and into mineralized bedrock. If Watson's observations hold true for termite mounds in other regions, then the sampling of these mounds may be a useful geochemical prospecting technique for locating buried mineral deposits, but only in areas where the soil or overburden is less than 3 m (10 ft) thick. This technique should be investigated further.

Animals can be considered to be one of many steps in the natural food chain and therefore in the geochemical cycle of many elements present in the chain. Species of animals that move about on land or in streams only within a limited area may well collect or concentrate chemical elements available to them in their food. If the source of food for these animals is already anomalous in trace metals, then these elements might be concentrated to an unusual extent in the tissue or in the waste products of the animals. Techniques that utilize animal tissue or waste products as geochemical sampling media are described below. However, the idea of killing wildlife solely for use in geochemical prospecting cannot be recommended and would never be condoned by conservation authorities.

The base-metal content of trout livers from lakes and streams in British Columbia was studied by Warren, Delavault, Fletcher, and Peterson (1971). They noted that plankton can concentrate heavy metals and that trout feed on these plankton. The authors concluded that it may sometimes be possible to use the base-metal content of samples of trout livers to detect anomalous concentrations of metals in an area.

Worthington (1968) described a study by the Colorado State Game, Fish, and Parks Department in which samples of deer antlers were collected at hunting check stations and were analyzed for gold in an attempt to discover new areas of potential gold resources. The results of the survey were not given; the approach, however, could easily be applied to the search for copper or other metal resources. Unfortunately, from a geochemical exploration standpoint, most deer range over wide areas; consequently, even if metal anomalies were detected in antlers, it might be difficult to identify the source areas.

In the arid lands of the Near East, much of the finer grained clastic overburden material has been transported great distances by the wind and is therefore not suitable as a geochemical sampling medium. In such areas, vegetation, although sparse, should be a useful sampling medium; however, regional custom dictates that living plant matter be saved for forage. Animals of the region, including camels, sheep, and goats, graze on the vegetation; consequently, animal dung may be an acceptable and useful sampling medium for regional reconnaissance in that part of the world (W. C. Overstreet, written commun., 1969).

Many fish-eating birds live in large rookeries along the seacoasts of the world. If the fish have ingested metal-rich food, then analyses for copper or other metals in samples of guano from the bird rookeries might indicate the locations of nearby metal-rich waters or seafloor deposits along coastlines.

Many endemic diseases of animals and man are now recognized as being related to excesses or deficiencies of trace elements in food or water. Webb (1971) described the use of stream-sediment chemical data to identify areas in England where livestock might be ingesting forage that contained excessive or insufficient concentrations of various trace elements known to affect animals. The reverse of Webb's approach might be a useful regional reconnaissance geochemical exploration technique; that is, it should be possible to locate areas containing anomalous concentrations of trace elements by locating areas high in incidence of trace-element associated endemic diseases of animals and man. Unfortunately, from an exploration standpoint, both man and animals are normally tolerant of anomalous amounts of copper (Scheinberg, 1970); however, excess amounts of other copper-related pathfinder elements do cause diseases. For example, the well-documented cattle disease molybdenosis (teart) is known to be related to the ingestion of excessive amounts of molybdenum. High concentrations of fluorine in drinking water cause mottling of human teeth. Other copper-related pathfinder elements that are thought to be detrimental to animals and man when present in anomalous amounts in the food chain might include lead, arsenic, mercury, cadmium, selenium, and probably others. It should be stressed that anomalous concentrations of trace elements can be caused by many natural and man-made factors. Therefore, the presence of any trace-element-related diseases within a region would not necessarily mean that the area in question has any potential for copper deposits. However, the application of this technique, especially in the less developed countries of the world, might prove fruitful.

ATMOSPHERE

The results of analyses of the gases in the atmosphere, and of the suspended particulate matter in the atmosphere, are proving valuable in geochemical exploration surveys for new mineral deposits. The detection of gases in the atmosphere can be accomplished by using gas-analysis instruments mounted in aircraft or in motor vehicles. McCarthy (1972) and Bristow and Jonasson (1972) have recently reviewed the use of airborne gas-analysis instruments for detecting mineral deposits, including those of copper. These authors noted that there are gases emanating from mineral deposits, and that these emanations can be detected in samples of the atmosphere collected above the deposits.

The application of chemical analyses of the element mercury in the search for mineral deposits has received the most attention in the literature to date, probably because mercury has a known close association with many types of sulfide mineral deposits, and because it is a very volatile element. Airborne gas analyzers have been used to detect mercury vapor in samples of the atmosphere collected above many different types of mineral deposits. McCarthy (1972) noted, however, that the concentrations of mercury in the atmosphere above porphyry copper deposits are apparently very low. He indicated that the measurement of mercury in the air above such deposits does not seem to be a useful means of detecting that type of copper deposit. The atmosphere above other types of copper deposits may contain higher levels of mercury. However, to date published data are not sufficient to indicate whether atmospheric mercury can be used to detect any type of copper deposit.

Anomalous amounts of sulfur dioxide, resulting from the oxidation of sulfide minerals, have been detected in samples of the atmosphere collected several metres above the Tyrone, N. Mex., porphyry copper deposit, as well as above other sulfide deposits (Rouse and Stevens, 1971). The chemical variations of sulfur dioxide concentrations in the atmosphere are therefore considered to be useful in the search for many types of sulfide deposits. Hydrogen sulfide should also be present wherever sulfide minerals are oxidizing and should be detectable in the atmosphere. Because the decomposition of organic matter can also produce gaseous sulfur species, anomalous concentrations of these compounds in the atmosphere must be carefully evaluated in order to determine the source of the gases.

Other gases have been found associated with various types of ore deposits. Fridman and Makhlova (1972) discussed the use of carbon dioxide as a geochemical indicator of mercury ores. In addition to CO_2, they detected nitrogen, hydrogen, helium, and argon in the vicinity of mercury ore. The work of Fridman and Makhlova was done underground; however, it does not seem unreasonable to expect that under the right conditions these same highly volatile species would reach the surface where they could escape and be detected in the atmosphere above the deposit.

Halogen gases are known to be associated with hydrothermal systems. The possibility of detecting anomalous amounts of these gases in the atmosphere above copper deposits has not been adequately tested as yet. McCarthy (1972), without giving details, noted that bromine and iodine have been detected in the air over a porphyry copper deposit in Arizona. Bristow and Jonasson (1972) also noted that iodine is associated both with porphyry copper deposits and with other types of base-metal deposits.

The decay of ^{40}K to ^{40}Ar might produce anomalous concentrations of argon in the atmosphere above zones of potassium metasomatism. This argon could be analyzed with appropriate airborne instrumentation.

Other gases might be detected in geochemical surveys using samples of the atmosphere above copper deposits. It is possible that the oxides of nitrogen could form in the zone of oxidation. And, as noted earlier, hydrocarbons, including methane and other compounds, have been found associated with ore deposits (Bristow and Jonasson, 1972; Shipulin and others, 1973). However, because many hydrocarbon compounds are formed from the decomposition of organic matter, nonsignificant anomalies may also be present. Lastly, there may be cases in which the relatively high vapor pressure of such normally nonvolatile elements as arsenic, antimony, selenium, tellurium, and perhaps others, would make it possible to detect these elements in the atmosphere above mineral deposits.

Plants are known to give off water vapor during transpiration. Continuing studies by the U.S. Geological Survey indicate that plants also exhale metallic compounds during transpiration (G. C. Curtin, oral commun., 1973). To date, the method has not been fully evaluated as a geochemical-prospecting technique (fig. 4); however, measurement of concentrations of trace metals in the air around plants may prove to be a useful technique for detecting anomalous amounts of metals in the soil in which the plants are rooted.

The results of analyses of particulate aerosols collected from 30 to 60 m (100 to 200 ft) above the ground were used effectively as a rapid regional geochemical exploration technique for detecting copper and other types of mineral deposits (Weiss, 1971). The distribution of the size of the particulate matter was found to be related to the distance from the source of the material. The technique was found to be effective except over areas covered by water, snow, or thick tropical forest.

REMOTE SENSING

In this report the term "remote sensing" is defined as (1) the quantitative or semiquantitative

FIGURE 4.—Plastic bags are attached to conifer trees to collect exudates for geochemical analysis. Alpine environment west of Denver, Colo. Photograph by G. C. Curtin, U.S. Geological Survey.

measurement of the chemical concentrations of one or more elements or compounds in material in situ, or (2) the measurement of chemical effects on vegetation as seen using photographs or other imagery. The remote-sensing instrument may be placed directly against (or very close to) the sample to be analyzed, or the instrument may be located at a distance of as much as several hundred kilometres from the sample site, as in the case of a satellite, but more likely at several thousands of metres, as from an aircraft. Remote-sensing geochemistry can be performed on land, in the air, and on or under bodies of water.

Neutron-activation analysis is a remote-sensing technique that has not been widely used in geochemical prospecting, probably because the necessary equipment is expensive and somewhat bulky. The method involves bombarding a sample with neutrons and then measuring the resulting gamma-ray spectrum. The technique is applicable to the detection of a number of elements, including copper. Because it measures the metal content in situ, this method offers two applications not readily available in other geochemical exploration techniques (Senftle, 1970). First, the apparatus can be adapted for down-the-hole measurements of various elements. The exact location and concentration of a given element can be readily determined. Second, the method offers means of locating copper or other metals beneath bodies of water. This second application could be particularly valuable as a relatively inexpensive method of evaluating the mineral potential of ocean or large-lake bottoms. Areas containing manganese nodules or other metal-rich sea-bottom deposits could be detected without having to collect a bottom or core sample for analysis at the surface.

The remote detection of natural gamma radiation using a sensitive airborne gamma-ray spectrometer has been described by Bennett (1971) and by Moxham, Foote, and Bunker (1965). The airborne spectrometer can detect natural gamma radiation emitted by potassium, uranium, and thorium. Several different types of copper deposits in Australia have been detected by this method (Bennett, 1971). Delineation of the widespread zone of potassium metasomatism commonly associated with porphyry-type copper deposits was accomplished at several Arizona copper deposits by Moxham, Foote, and Bunker (1965). They also noted that potassium-thorium ratios should be valuable in delineating altered rock masses.

Aerial photography appears to be a useful remote-sensing method for detecting and evaluating geobotanical and biogeochemical anomalies associated with base-metal mineral deposits, especially in areas with heavy vegetative growth. Ordinary color photography could be used to detect the presence or absence of, and the areal extent of, specific plants or plant communities. In addition, low-level color photography could be used to detect indicator plants during their flowering period. From altitudes of about 150 to 300 m (500 to 1,000 ft) above the ground, I have observed the colorful blooms of the California poppy (*Eschscholtzia mexicana*) growing in masses over known copper deposits in Arizona. Areas containing these flowers should be detectable on color aerial photographs taken at similar altitudes.

Infrared color film has been used to detect vegetation that is unhealthy because of disease or insect damage. Some types of vegetation, however, become stressed because of an abnormal enrichment or depletion of trace elements in the material in which they are rooted (F. C. Canney, oral commun., 1972).

Plants growing in metal-enriched soils have spectral properties that may be detectable from remote locations either by using infrared film or by using some sort of spectral scanning instrument (Marshall, 1970a; Press and Norman, 1972). In regions containing deep-rooted plants, such instrumentation could be used to detect metal anomalies in bedrock covered by relatively thin layers of transported overburden. Studies of the spectral properties of plants would therefore be especially valuable in the search for copper deposits buried by glacial debris or by gravel deposits such as those commonly present on the desert pediments in the porphyry-copper province of the southwestern United States. The technique could also be used over areas of dense vegetation, such as tropical jungles, where bedrock cannot be readily sampled and little or no outcrop can be seen on aerial photographs.

The stunting or low density of vegetation in some areas may be caused by high metal concentrations in the associated soils. Areas showing these effects should be readily visible on either color or black-and-white aerial photographs. Many humid tropical areas, however, are commonly covered with clouds for much of the year and are therefore not suitable for normal aerial photography. The effects of metal stress on vegetation in such areas might be evaluated by using airborne radar imagery. This imagery can be obtained through cloud cover and could be used to map the general height of the forest canopy and the density of growth in an area (F. C. Canney, oral commun., 1973).

STATISTICS

INTRODUCTION

The most easily discovered metal deposits have already been found in most parts of the world. In the future, scientists will be looking for ways to distinguish subtle geochemical anomalies of possible economic significance from increasingly complex geochemical background data. Today we are trying not only to discriminate between natural metal anomalies and natural background populations, but also to distinguish between these natural populations and man-made populations caused by contamination and pollution. Clearly, new approaches to geochemical exploration are needed. The use of statistical techniques is one example. Various fields within the social, biological, and electrical engineering sciences have provided the basic statistical techniques that are now being adapted to problems in the interpretation of geochemical data.

It should be stressed that the ultimate evaluation of any computer output must be related back to the real world of natural systems; in other words, the data output is only as good as the data input. In short, the computer supplements but does not replace the geochemist.

Statistical treatment of geochemical data was necessarily limited before the advent of computers for data processing. Most precomputer statistical evaluations were limited to the determination of such parameters as mean, median, and standard deviation in order to establish the limits of background and anomalous populations. Graphical distributions of data sets were also studied and indicated that, in general, the analyses of a given population follow more closely a lognormal distribution than a normal one. As with any natural system, exceptions to this generalization are known. Ratios of elements to each other, to regional background, or to Clarke values have also been helpful for showing trends of elements both laterally and with depth. In the field or in localities where computers are not available, geochemists have determined threshold values and the ranges of background and anomalous values for even large data sets using cumulative frequency plots (Lepeltier, 1969).

Precomputer statistical analyses of geochemical data sets were generally limited to the use of only one variable at a time (univariate analysis). The advent of computer data processing means that several or many geochemical variables can be studied simultaneously (multivariate analysis). In addition to studying the chemical data of a sample, geochemists can now compare conditions of the physical and chemical environment of the sample site or region with the sample analytical data. In short, computer processing of data has opened up a wide range of possibilities for evaluating geochemical data.

In the following discussion, some examples are given of how statistical interpretation techniques might be applied to geochemical data. Several detailed reviews of this field have been published recently (Marshall, 1970b; Agterberg and Kelly, 1971; Rose, 1972; Nichol, 1973). The reader is referred to these papers for more specific applications of the techniques to geochemical exploration programs.

CORRELATION ANALYSIS

A simple correlation analysis measures the degree of association between two or more variables taken two at a time. A multiple correlation analysis measures the combined effect of several variables on a selected variable. Correlation analysis could be valuable, for example, in determining which elements or other variables associate most closely with copper in any given sampling medium. Elements that are found to have a high degree of positive or negative correlation with copper might serve as pathfinder elements in an area under study.

REGRESSION ANALYSIS

Regression analysis attempts to equate mathematically one variable (the dependent variable) with a group of other variables (the independent variables). When only two variables are used, the analysis is called a simple regression analysis; when more than two variables are involved, the analysis is called a multiple regression analysis. The technique has been used in surveys to explain the variation of a given element in terms of other elements and of other physical and chemical factors. For example, the variation of the concentration of copper in a stream-sediment sample could be compared with such other variables as (1) the concentrations of other elements in the sample; (2) the grain size of the sample material; (3) the mineralogical composition of the sample; (4) the pH of the stream water; or (5) the width, depth, and velocity of the stream, in an attempt to determine which factors significantly influence the variability of copper in the sample and the relative importance of each factor. Once an equation for a given data set has been determined, regression analysis can be used to calculate, for example, the theoretical copper concentration at a given site based on the independent variables for that site. The differences between the calculated copper concentrations and the measured copper concentrations, called residual values, can then be computed. One can then study both the residual data and the theoretical data in an effort to find sites containing ore-related anomalies that could not be found using only the raw data.

DISCRIMINANT ANALYSIS

Discriminant analysis is a classification scheme for studying geochemical data. A commonly used type of discriminant analysis creates and uses a mathematical equation based on some combination of variables to maximize the differences between two populations. This technique requires data on two different populations to begin with. New data are mathematically compared with these two populations and then assigned to one or the other on the basis of all similarities and differences. An ideal example of application of this method would be one in which there were, for a given area, a data set from a mineralized sample population and a data set from a background sample population. These data sets could be acquired in an orientation study. Equations derived from these two populations could then be compared with new data from samples collected for the entire survey to determine whether individual sites in the extended survey more closely represented anomalous or background conditions.

FACTOR ANALYSIS

Factor analysis is a method for identifying common factors in the variables of a data set. A factor analysis program starts with a matrix of values similar to a correlation matrix of geochemical data and assigns the various elements of the matrix to groups (factors) based on a common variability of these elements.

A Q-mode factor analysis investigates the interrelationships between samples. The analysis compares the set of variables at each sample site with those at every other site and groups the samples into a smaller number of "typical" samples. From this technique, the relationship between samples may be deduced. Q-mode factor analysis can be used, for example, to group data in terms of geologic parameters such as bedrock types.

An R-mode factor analysis investigates the interrelationships between variables. This type of analysis groups chemical data that vary sympathetically in all samples into a set of factors, each containing one or more of the original variables. R-mode factor analysis can be used to identify groups of elements that have common associations; for example, this technique can be used to find those elements that would be scavenged by the manganese and iron oxides found in stream sediments.

CLUSTER ANALYSIS

Multi-element data sets can also be classified into groups by the use of cluster analysis. A commonly used version of this technique, which can also be done in a Q- or R-mode, compares pairs of variables or samples, or pairs of pairs, and so on, and then arranges these pairs (clusters) into a hierarchical dendritic diagram (dendogram) in which the variables or samples are grouped according to levels of pairing. These levels are based on values for correlation coefficients between cluster pairs. As an example, the method could be applied to a data set in an attempt, on the basis of selected chemical associations, to separate clusters representing samples from mineralized areas and those representing samples from background areas.

TREND-SURFACE ANALYSIS

The preceding methods have dealt mainly with analysis of numerical geochemical data in order to find common associations as an aid to interpreting the data. Several techniques are also available for showing objectively, in the form of a map, the spatial distribution of geochemical data. These methods are especially applicable to large data sets from samples collected from large regions. Trend-surface analysis is similar to multiple-regression analysis but involves the fitting of mathematical surfaces to data. In trend-surface analysis the dependent variable, a chemical or geologic variable, is equated mathematically to geographic coordinates. The variation of this dependent variable over the region sampled defines a mathematical equation representing a plane or curved (trend) surface. This trend surface can be contoured for study in a manner similar to a topographic contour map. The mathematical equation for any trend surface can be expanded within practical limits by adding several more terms to the equation. This addition has the effect mathematically of more precisely defining the variations in the dependent variable. Visually, the effect of adding more terms is a more detailed contouring of the map.

Trend-surface analysis should be valuable in studying the changes in a given variable such as copper content, over an area of any size; however, adequate data-point distribution is imperative if the method is to succeed. As is the case with multiple-regression analysis, trend-surface analysis can be used to compute theoretical values at each sample site, based on regional trends, to compare with the actual measured values at the site. The difference between the theoretical and measured values at a given site is the residual value for that site. Residual values can be plotted and contoured for data evaluation. In a manner similar to that used in regression analysis, residuals can be used to remove regional geochemical trends from local variations. Theoretically, the residuals should then delineate anomalous areas that might be related to mineral deposits. Unfortunately, in natural systems, chemical trends are seldom regular enough to make use of this method without taking into account other geological and chemical information.

MOVING-AVERAGE ANALYSIS

The moving-average analysis (also called a rolling mean analysis) is another popular technique for treating data spatially. In this technique, a search area large enough to include several data points on a map is moved across the map. Values within the search area at any given time are averaged, and the mean value is plotted in the center of the search area. The degree of smoothing of the original data can thus be varied by changing the size or degree of overlap of the search area and by changing the manner of weighting and averaging the data within the search area. The technique can be used to smooth regional geochemical data in order to enhance regional geochemical trends because the technique tends to remove anticipated sampling and analytical noise from geochemical data.

In a manner similar to other computer analytical techniques, this technique can be used to calculate residuals, the differences between the smoothed mean value and the measured value at any point on the map of the study area. These residuals can then be contoured and used in evaluating the study area.

REFERENCES CITED

Agterberg, F. P., and Kelly, A. M., 1971, Geomathematical methods for use in prospecting: Canadian Mining Jour., v. 92, no. 5, p. 61–72.

Al'bov, M. N., and Kostarev, I. I., 1968, Copper in the peat bog formations of the Middle Ural [In Russian]: Sovetskaya Geologiya, v. 11, no. 2, p. 132–139; English abs. in Chem. Abs., v. 68, abs. no. 106804, 1968.

Al-Hashimi, A. R. K., and Brownlow, A. H., 1970, Copper content of biotites from the Boulder Batholith, Montana: Econ Geology, v. 65, no. 8, p. 985–992.

Allan, R. J., 1971, Lake sediment—a medium for regional geochemical exploration of the Canadian Shield: Canadian Mining and Metall. Bull., v. 64, no. 715, p. 43–59.

Allan, R. J., Cameron, E. M., and Durham, C. C., 1973, Reconnaissance geochemistry using lake sediments of a 36,000-square-mile area of the northwestern Canadian Shield: Canada Geol. Survey Paper 72–50, 70 p.

Allan, R. J., and Crook, R. T., 1972, Lake sediments from permafrost regions—Zn, Cu, Ni, Co, and Pb content of the sub-2000 micron particle size ranges, *in* Geological Survey of Canada, Report of activities, Pt. B, November, 1971 to March, 1972: Canada Geol. Survey Paper 72–1, p. 31–37.

Allan, R. J., and Hornbrook, E. H. W., 1971, Exploration geochemistry evaluation study in a region of continuous permafrost, Northwest Territories, Canada, *in* Geochemical exploration (Internat. Geochemical Explor. Symposium, 3d, Proc.): Canadian Inst. Mining and Metallurgy Spec. Vol. 11, p. 53–66.

Allan, R. J., Lynch, J. J., and Lund, N. G., 1972, Regional geochemical exploration in the Coppermine River area, District of Mackenzie—a feasibility study in permafrost terrain: Canada Geol. Survey Paper 71–33, 52 p.

Awald, J. T., 1971, Regional geochemical reconnaissance of the Bradshaw Mountains, Arizona: Am. Inst. Mining, Metall., and Petroleum Engineers Trans., v. 250, no. 2, p. 114–119.

Bell, Henry, and Hornig, C. A., 1970, Use of iron-oxide pseudomorphs after pyrite in geochemical prospecting: U.N. ECAFE Mineral Resources Devel. Ser. 38, p. 127–129 [*See* United Nations entry.]

Bennett, Richmond, 1971, Exploration for hydrothermal mineralization with airborne geochemistry: Am. Inst. Mining, Metall., and Petroleum Engineers Trans., v. 250, no. 2, p. 109–113.

Boyle, R. W., and Dass, A. S., 1967, Geochemical prospecting—use of the A horizon in soil surveys: Econ. Geology, v. 62, no. 2, p. 274–276.

Boyle, R. W., Hornbrook, E. H. W., Allan, R. J., Dyck, W., and Smith, A. Y., 1971, Hydrogeochemical methods—application in the Canadian Shield: Canadian Mining and Metall. Bull., v. 64, no. 715, p. 60–71.

Boyle, R. W., Tupper, W. M., Lynch, J., Friedrich, G., Ziauddin, M., Shafiquallah, M., Carter, M., and Bygrave, K., 1966, Geochemistry of Pb, Zn, Cu, As, Sb, Mo, Sn, W, Ag, Ni, Co, Cr, Ba, and Mn in the waters and stream sediments of the Bathurst-Jacquet River district, New Brunswick: Canada Geol. Survey Paper 65–42, 50 p.

Bradshaw, P. M. D., Clews, D. R., and Walker, J. L., 1970a, Exploration geochemistry, Pt. 2, Detailed surveys: Mining in Canada, 1970, February, p. 22–32.

——— 1970b, Exploration geochemistry, Pt. 3, Regional surveys: Mining in Canada, 1970, April, p. 13–21.

——— 1971, Exploration geochemistry, Pt. 6, Areas of continental glaciation: Canadian Mining Jour., v. 92, no. 12, p. 29–38.

——— 1972, Exploration geochemistry, Pt. 7, Canadian problem—valley glaciated and non-glaciated areas: Canadian Mining Jour., v. 93, no. 5, p. 53–64 and p. 85.

Bristow, Q., and Jonasson, I. R., 1972, Vapor sensing for mineral exploration: Canadian Mining Jour., v. 93, no. 5, p. 39–47 and p. 85.

Brock, J. S., 1972, The use of dogs as an aid to exploration for sulfides: Western Miner, v. 45, no. 12, p. 28–32.

Brooks, R. R., 1972, Geobotany and biogeochemistry in mineral exploration: New York, Harper and Row, 290 p.

Brown, R. G., 1970, Geochemical survey of the vicinity of Oracle, Arizona: Arizona State Univ., unpub. M.S. thesis, 56 p.

Brundin, N. H., and Nairis, B., 1972, Alternative sample types in regional geochemical prospecting: Jour. Geochem. Explor., v. 1, no. 1, p. 7–46.

Burnham, C. W., 1959, Metallogenic provinces of the southwestern United States and northern Mexico: New Mexico Bur. Mines and Mineral Resources Bull. 65, 76 p.

Cannon, H. L., 1960, Botanical prospecting for ore deposits: Science, v. 132, no. 3427, p. 591–598.

——— 1971, The use of plant indicators in ground water surveys, geologic mapping, and mineral prospecting: Taxon, v. 20, no. 2–3, p. 227–256.

Chaffee, M. A., Botbol, J. M., and Hamilton, J. C., 1972, The distribution of selected elements in stream sediments, central Maine: U.S. Geol. Survey open-file rept., 8 p.

Chaffee, M. A., and Hessin, T. D., 1971, An evaluation of geochemical sampling in the search for concealed "porphyry" copper-molybdenum deposits on pediments in southern Arizona, *in* Geochemical exploration (Internat. Geochemical Explor. Symposium, 3d, Proc.): Canadian Inst. Mining and Metallurgy Spec. Vol. 11, p. 401–409.

Chamberlain, T. C., 1883, Terminal moraine of the second glacial epoch: U.S. Geol. Survey Third Ann. Rept., p. 291–402.

Chitayeva, N. A., Miller, A. D., Grosse, Yu. I., and Christyakova, N. I., 1971, Iodine distribution in the supergene zone of the Gay chalcopyrite deposit: Geochemistry Internat., v. 8, no. 3, p. 426–436.

Coolbaugh, D. F., 1971, La Caridad, Mexico's newest and largest porphyry copper deposit—an exploration case history: Am. Inst. Mining, Metall., and Petroleum Engineers Trans., v. 250, no. 2, p. 133–138.

Coope, J. A., 1973, Geochemical prospecting for porphyry copper-type mineralization—a review: Jour. Geochem. Explor., v. 2, no. 2, p. 81–102.

Curtin, G. C., Lakin, H. W., Hubert, A. E., Mosier, E. L., and Watts, K. C., 1971, Utilization of mull (forest humus layer) in geochemical exploration in the Empire district, Clear Creek County, Colorado: U.S. Geol. Survey Bull. 1278–B, 39 p.

de Grys, Ann, 1970, Copper and zinc in alluvial magnetites from central Ecuador: Econ. Geology, v. 65, no. 6, p. 714–717.

Dreimanis, A., 1958, Tracing ore boulders as a prospecting method in Canada: Canadian Inst. Mining and Metallurgy Bull., v. 51, no. 550, p. 73–80.

Dyck, W., Dass, A. S., Durham, C. C., Hobbs, J. D., Pelchat, J. C., and Galbraith, J. H., 1971, Comparison of regional geochemical uranium exploration methods in the Beaverlodge Area, Saskatchewan, *in* Geochemical Exploration (Internat. Geochemical Explor. Symposium, 3d, Proc.): Canadian Inst. Mining and Metallurgy Spec. Vol. 11, p. 132–150.

Engel, C. G., and Sharp, R. P., 1958, Chemical data on desert varnish: Geol. Soc. America Bull., v. 69, no. 5, p. 487–518.

Erickson, R. L., Marranzino, A. P., Oda, Uteana, and Janes, W. W., 1966, Geochemical reconnaissance in the Pequop Mountains and Wood Hills, Elko County, Nevada: U.S. Geol. Survey Bull. 1198–E, 20 p.

Fisher, N. H., 1970, Recent research in geochemical prospecting in Australia: U.N. ECAFE Mineral Resources Devel. Ser. 38, p. 68–72. [*See* United Nations entry.]

Fridman, A. I., and Makhlova, N. K., 1972, Certain aspects of origin and migration of carbon dioxide in mercury deposits, as in the Nikitovka, Donbass: Internat. Geology Rev., v. 14, no. 12, p. 1345–1350.

Garrett, R. G., 1971, The dispersion of copper and zinc in glacial overburden at the Louvem deposit, Val d'Or, Quebec, *in* Geochemical exploration (Internat. Geochemical Explor. Symposium, 3d, Proc.): Canadian Inst. Mining and Metallurgy Spec. vol. 11, p. 157–158.

Giles, D. L., and Schilling, J. H., 1972, Variation in rhenium content of molybdenite, *in* Geochemistry: Internat. Geol. Cong., 24th, Montreal, 1972, Proc., sec. 10, p. 145–152.

Ginzburg, I. I., 1960, Principles of geochemical prospecting [orig. in Russian]: New York, Pergamon Press, 311 p.

Gleeson, C. F., and Coope, J. A., 1967, Some observations on the distribution of metals in swamps in eastern Canada, *in* Cameron, E. M., ed., Symposium on geochemical prospecting Ottawa, 1966, Proc.: Canada Geol. Survey Paper 66–54, p. 145–166.

Govett, G. J. S., and Hale, W. E., 1967, Geochemical orientation and exploration near a disseminated copper deposit, Luzon, Philippines: Inst. Mining and Metallurgy Trans., sec. B, v. 76, no. 732, p. B190–B201.

Griffitts, W. R., and Alminas, H. V., 1968, Geochemical evidence for possible concealed mineral deposits near the Monticello Box, northern Sierra Cuchillo, Socorro County, New Mexico: U.S. Geol. Survey Circ. 600, 13 p.

Hamil, B. M., and Nackowski, M. P., 1971, Trace-element distribution in accessory magnetite from quartz monzonite intrusives and its relation to sulfide mineralization in the Basin and Range province of Utah and Nevada—a preliminary report, *in* Geochemical exploration (Internat. Geochemical Explor. Symposium, 3d, Proc.): Canadian Inst. Mining and Metallurgy Spec. Vol. 11, p. 331–333.

Hawkes, H. E., and Webb, J. S., 1962, Geochemistry in mineral exploration: New York, Harper and Row, 415 p.

Holmes, R., and Tooms, J. S., 1973, Dispersion from a submarine exhalative ore body: Internat. Geochem. Explor. Symposium, 4th, London, 1972, Proc., p. 193–202.

Hornbrook, E. H. W., and Allan, R. J., 1970, Geochemical exploration feasibility study within the zone of continuous permafrost, Coppermine River region, Northwest Territories: Canada Geol. Survey Paper 70–36, 35 p.

Huff, L. C., 1955, A Paleozoic geochemical anomaly near Jerome, Arizona: U.S. Geol. Survey Bull. 1000–C, p. 105–118.

——— 1970, A geochemical study of alluvium-covered copper deposits in Pima County, Arizona: U.S. Geol. Survey Bull. 1312–C, 31 p.

——— 1971, A comparison of alluvial exploration techniques for porphyry copper deposits, *in* Geochemical exploration (Internat. Geochemical Explor. Symposium, 3d, Proc.): Canadian Inst. Mining and Metallurgy Spec. Vol. 11, p. 190–194.

Jenne, E. A., 1968, Controls on Mn, Fe, Co, Ni, Cu, and Zn concentrations in soils and water—the significant role of hydrous Mn and Fe oxides, *in* Trace inorganics in water: Advances in Chemistry Ser. 73, p. 337–387.

Jerome, S. E., 1966, Some features pertinent in exploration of porphyry copper deposits, *in* Titley, S. R., and Hicks, C. L., eds., Geology of the porphyry copper deposits, southwestern North America: Tucson, Ariz., Arizona Univ. Press, p. 75–85.

Jonasson, I. R., and Allan, R. J., 1973, Snow—a sampling medium in hydrogeochemical prospecting in temperate and permafrost regions: Internat. Geochem. Explor. Symposium, 4th, London, 1972, Proc., p. 161–176.

Kleinkopf, M. D., 1960, Spectrographic determination of trace elements in lake waters of northern Maine: Geol. Soc. America Bull., v. 71, no. 8, p. 1231–1242.

Kravtsov, A. I., and Fridman, A. I., 1965, Natural gases of ore deposits [in Russian]: Akad. Nauk SSSR Doklady, v. 165, no. 5, p. 1168–1170; translated in Acad. Sci. U.S.S.R. Doklady, Earth Sci. Sec., v. 165, nos. 1–6, p. 192–193. [1966].

Kuznetsov, S. I., Ivanov, M. V., and Lyalikova, N. N., 1963, Introduction to geological microbiology (translated from 1962 Russian edition): New York, McGraw-Hill Book Co., 252 p.

Lakin, H. W., Hunt, C. B., Davidson, D. F., and Oda, Uteana, 1963, Variation in minor-element content of desert varnish: U.S. Geol. Survey Prof. Paper 475–B, p. B28–B31.

Learned, R. E., and Boissen, Rafael, 1973, Gold—a useful pathfinder element in the search for porphyry copper deposits in Puerto Rico: Internat. Geochem. Explor. Symposium, 4th, London, 1972, Proc., p. 93–104.

Lee, H. A., 1965, 1.—Investigations of eskers for mineral exploration: Canada Geol. Survey Paper 65–14, p. 1–17.

———, 1971, Mineral discovery in the Canadian Shield using the physical aspects of overburden: Canadian Mining and Metall. Bull., v. 64, no. 715, p. 32–36.

Lee, K. E., and Wood, T. G., 1971, Termites and soils: New York, Academic Press, 251 p.

Lepeltier, C., 1969, A simplified statistical treatment of geochemical data by graphical representation: Econ. Geology, v. 64, no. 5, p. 538–550.

Levinson, A. A., 1974, Introduction to exploration geochemistry: Calgary, Applied Publishing Ltd., 612 p.

Lovering, T. G., Cooper, J. R., Drewes. Harald, and Cone, G. C., 1970, Copper in biotite from igneous rocks in southern Arizona as an ore indicator: U.S. Geol. Survey Prof. Paper 700–B, p. B1–B8.

Lovering, T. S., Huff, L. C., and Almond, Hy., 1950, Dispersion of copper from the San Manuel copper deposit, Pinal County, Arizona: Geol. Soc. America Bull., v. 45, no. 6, p. 493–514.

Lundqvist, Jan, 1967, Physiography of Sweden, *in* Kvalheim, Aslak, ed., Geochemical prospecting in Fennoscandia: New York, Interscience Publishers, p. 69–84.

Marshall, N. J., 1970a, Applications of aerial photography in regional geologic mapping: U.N. ECAFE Mineral Resources Devel. Ser. 38, p. 257–262. [*See* United Nations entry.]

——— 1970b, Geostatistics in geochemical exploration—a review: U.N. ECAFE Mineral Resources Devel. Ser. 38, p. 314–340. [*See* United Nations entry.]

McCarthy, J. H., Jr., 1972, Mercury vapor and other volatile components in the air as guides to ore deposits: Jour. Geochem. Explor., v. 1, no. 2, p. 143–162.

Mehrtens, M. B., Tooms, J. S., and Troup, A. G., 1973, Some aspects of geochemical dispersion from base-metal mineralization within glaciated terrain in Norway, North Wales, and British Columbia, Canada: Internat. Geochem. Explor. Symposium, 4th, London, 1972, Proc., p. 105–115.

Moxham, R. M., Foote, R. S., and Bunker, C. M., 1965, Gamma-ray spectrometer studies of hydrothermally altered rocks: Econ. Geology, v. 60, no. 4, p. 653–671.

Nesvetaylova, N. G., 1961, Geobotanical investigations in prospecting for ore deposits: Internat. Geology Rev., v. 3, no. 7, p. 609–618.

Nichol, Ian, 1973, The role of computerized data systems in geochemical exploration: Canadian Inst. Mining and Metallurgy Bull., v. 66, no. 729, p. 59–68.

Nilsson, Gunnar, 1971, The use of dogs in prospecting for sulfide ores [in English]: Geol. Fören. Stockholm Förh., v. 93, p. 725–728.

Ovchinnikov, L. N., Sokolov, V. A., Fridman, A. I., and Yanitskii, I. N., 1973, Gaseous geochemical methods in structural mapping and prospecting for ore deposits: Internat. Geochem. Explor. Symposium, 4th, London, 1972, Proc., p. 177–182.

Parry, W. T., and Nackowski, M. P., 1963, Copper, lead, and zinc in biotites from basin and range quartz monzonites: Econ. Geology v. 58, no. 7, p. 1126–1144.

Perhac, R. M., and Whelan, C. J., 1972, A comparison of water, suspended solid and bottom sediment analyses for geochemical prospecting in a northeast Tennessee zinc district: Jour. Geochem. Explor., v. 1, no. 1, p. 47–53.

Phillips, W. S., 1963, Depth of roots in soil: Ecology, v. 44, no. 2, p. 424.

Post, E. V., and Hite, J. B., 1964, Heavy metals in stream sediment, west-central Maine [rev. ed.]: U.S. Geol. Survey Mineral Inv. Field Studies Map MF–278.

Press, N. P., and Norman, J. W., 1972, Detection of ore bodies by remote-sensing the effects of metals on vegetation: Inst. Mining and Metallurgy Trans., Sec. B, v. 81, no. 789, p. B166–B168.

Putman, G. W., and Burnham, C. W., 1963, Trace elements in igneous rocks, northwestern and central Arizona: Geochim. et Cosmochim. Acta, v. 27, no. 1, p. 53–106.

Rehrig, W. A., and Heidrick, T. L., 1972, Regional fracturing in Laramide stocks of Arizona and its relationship to porphyry copper mineralization: Econ. Geology, v. 67, no. 2, p. 198–213.

Rose, A. W., 1972, Statistical interpretation techniques in geochemical exploration: Am. Inst. Mining, Metall., and Petroleum Engineers Trans., v. 252, no. 3, p. 233–239.

Rouse, G. E., and Stevens, D. N., 1971, The use of sulfur dioxide gas geochemistry in the detection of sulfide deposits: Golden, Colo., Earth Sciences Inc., 2 p.

Rubo, G. L., 1969, Certain features in zonation of dispersion halos of Akhtal barite-polymetallic ore deposit, northern Armenia: Internat. Geology Rev., v. 11, no. 2, p. 203–208.

Sakrison, H. C., 1971, Rock geochemistry—its current usefulness on Canadian Shield: Canadian Mining and Metall. Bull., v. 64, no. 715, p. 28–31.

Salmi, Martti, 1967, Peat in prospecting—applications in Finland, *in* Kvalheim, Aslak, ed., Geochemical prospecting in Fennoscandia: New York, Interscience Publishers, p. 113–126.

Scheinberg, I. H., 1970, The essentiality and toxicity of copper in man. *in* Hemphill, D. D., ed., Trace substances in environmental health——3 [3d Ann. Conf., Proc.]: Columbia, Missouri Univ., p. 79–82.

Senftle, F. E., 1970, Mineral exploration by nuclear techniques: Mining Cong. Jour., v. 56, no. 1, p. 21–28.

Shilts, W. W., 1971, Till studies and their application to regional drift prospecting: Canadian Mining Jour., v. 92, no. 4, p. 45–50.

Shipulin, F. K., Genkin, A. D., Distler, V. V., Komarov, P. V., Malinkovskii, E. P., Ozerova, N. A., Perel'man, A. I., Rekharskii, V. I., Rozanov, Yu. A., Filimonova, L. G., Chernyshev, V. F., and Elinson, M. M., 1973, Some aspects of the problem of geochemical methods of prospecting for concealed mineralization: Jour. Geochem. Explor., v. 2, no. 3, p. 193–235.

Shvartsev, S. L., 1972a, Hydrogeochemical prospecting for blind ores in permafrost: Internat. Geology Rev., v. 14, no. 10, p. 1037–1043.

——— 1972b, Geochemical prospecting methods in the regions of permanently frozen ground, *in* Geochemistry: Internat. Geol. Cong., 24th, Montreal, 1972, Proc., sec. 10, p. 380–384.

Smith, A. R., 1970, Trace elements in the Plumas copper belt, Plumas County, California: California Div. Mines and Geology Spec. Rept. 103, 26 p.

Stirling, J., 1972. Man's best friend to replace him?: Canadian Mining Jour., v. 93, no. 11, p. 60–61.

Tan, Li-Ping, and Yu, Fang-Sung, 1968, Heavy-mineral reconnaissance for gold and copper deposits of the Chinkuashih area, Taiwan [in English]: Acta Geol. Taiwanica, no. 12, p. 41–57.

Timperley, M. H., Jonasson, I. R., and Allan, R. J., 1973, Subaquatic organic gels—a medium for geochemical prospecting in the southern Canadian Shield, *in* Geological Survey of Canada, Report of activities, Part A—April to October 1972: Canada Geol. Survey Paper 73–1, pt. A, p. 58–62.

United Nations, 1970, Proceedings of the second seminar on geochemical prospecting methods and techniques, Ceylon, 1970: Econ. Comm. for Asia and the Far East [ECAFE], Mineral Resources Devel. Ser. 38, 413 p.

Warren, H. V., and Delavault, R. E., 1960, Aqua regia extractable copper and zinc in plutonic rocks in relation to ore deposits: Inst. Mining and Metallurgy Bull. 643, p. 495–504.

——— 1969, Aqua regia extractable copper and zinc in volcanic rocks in relation to copper mineralization: Econ. Geology, v. 64, no. 6, p. 672–676.

Warren, H. V., Delavault, R. E., Fletcher, K., and Peterson, G. R., 1971, The copper, zinc and lead content of trout livers as an aid in the search for favourable areas to prospect, *in* Geochemical exploration (Internat. Geochemical Explor. Symposium, 3d, Proc.): Canadian Inst. Mining and Metallurgy Spec. Vol. 11, p. 444–450.

Warren, H. V., Delavault, R. E., and Irish, R. I., 1949, Biogeochemical researches on copper in British Columbia: Royal Soc. Canada Trans., 3d ser., v. 43, sec. 4, p. 119–137.

——— 1951, Further biogeochemical data from the San Manuel copper deposit, Pinal County, Arizona: Geol. Soc. America Bull., v. 62, no. 8, p. 919–930.

Warren, H. V., and Howatson, C. H., 1947, Biogeochemical prospecting for copper and zinc [British Columbia]: Geol. Soc. America Bull., v. 58. no. 9, p. 803–820.

Watson, J. P., 1970, Contribution of termites to development of zinc anomaly in Kalahari sand: Inst. Mining and Metallurgy Trans., Sec. B, v. 79, no. 762, p. B53–B59.

——— 1972, The distribution of gold in termite mounds and soils at a gold anomaly in Kalahari sand: Soil Sci., v. 113, no. 5, p. 317–321.

Webb, J. S., 1971, Regional geochemical reconnaissance in medical geography, *in* Cannon, H. L., and Hopps, H. C., eds., Environmental geochemistry in health and disease: Geol. Soc. America Mem. 123, p. 31–42.

Weiss, O., 1971, Airborne geochemical prospecting, *in* Geochemical exploration (Internat. Geochemical Explor. Symposium, 3d, Proc.): Canadian Inst. Mining and Metallurgy Spec. Vol. 11, p. 502–514.

Weissberg, B. G., 1969, Gold-silver ore-grade precipitates from New Zealand thermal waters: Econ. Geology, v. 64, no. 1, p. 95–108.

White, D. E., 1967, Mercury and base-metal deposits with associated thermal and mineral waters, *in* Barnes, H. L., ed., Geochemistry of hydrothermal ore deposits: New York, Holt, Rinehart and Winston, p. 575–631.

Wolfe, W. J., 1971, Biogeochemical prospecting in glaciated terrain of the Canadian Precambrian Shield: Canadian Mining and Metall. Bull., v. 64, no. 715, p. 72–80.

Worthington, J. E., 1968, Rock in the box: Mining Eng., v. 20, no. 1, p. 49.

☆U.S. GOVERNMENT PRINTING OFFICE: 1975 O—211-317/17