Principles of Geochemical Prospecting

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CONTRIBUTIONS TO GEOCHEMICAL PROSPECTING FOR MINERALS

PRINCIPLES OF GEOCHEMICAL PROSPECTING

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ABSTRACT

Geochemical prospecting for minerals includes any method of mineral exploration based on systematic measurement of the chemical properties of a naturally occurring material. The purpose of the measurements is the location of geochemical anomalies or of areas where the chemical pattern indicates the presence of ore in the vicinity. Anomalies may be formed either at depth by igneous and metamorphic processes or at the earth's surface by agents of weathering, erosion, and surficial transportation.

Geochemical anomalies of deep-seated origin—primary anomalies—may result from (1) apparent local variation in the original composition of the earth's crust, defining a distinctive "geochemical province" especially favorable for the occurrence of ore, (2) impregnation of rocks by mineralizing fluids related to ore formation, and (3) dispersion of volatile elements transported in gaseous form.

Anomalies of surficial origin—secondary anomalies—take the form either of residual materials from weathering of rocks and ores in place or of material dispersed from the ore deposit by gravity, moving water, or glacial ice. The mobility of an element, or tendency for it to migrate in the surficial environment, determines the characteristics of the geochemical anomalies it can form. Water is the principal transporting agency for the products of weathering. Mobility is, therefore, closely related to the tendency of an element to be stable in water-soluble form. The chemical factors affecting the mobility of elements include hydrogen-ion concentration, solubility of salts, coprecipitation, sorption, oxidation potential, and the formation of complexes and colloidal solutions. The mobility of the elements may be further modified by biological factors.

Secondary anomalies may occur in residual materials or in materials transported by ice, frost, underground water, animals, soil-forming processes, plant activity, and surface water. Each one of these transporting agencies gives a characteristic distribution pattern to the weathering products of ore deposits.

Geochemical methods have been applied most extensively in the Soviet Union, Scandinavia, the United States, Canada, Africa, and Japan. The most uniformly successful geochemical prospecting work has been based on sampling and analysis of residual soil and vegetation; anomalies caused by movement of metals in ground and surface water show promise as an effective means of locating buried ore deposits. Some suggestions for the execution of geochemical surveys and the interpretation of geochemical data in terms of possible ore are presented.

INTRODUCTION

Geochemical prospecting for minerals, as defined by common usage, includes any method of mineral exploration based on systematic measurement of one or more chemical properties of a naturally occurring material. The chemical property measured is most commonly the trace content of some element or group of elements; the naturally occurring material may be rock, soil, gossan, glacial debris, vegetation, stream sediment, or water. The purpose of the measurements is the discovery of a geochemical "anomaly" or area where the chemical pattern indicates the presence of ore in the vicinity.

The broader science of geochemistry, as originally defined by Goldschmidt and summarized by Mason (1952, p. 2), is concerned with:

> 1. The determination of the relative and absolute abundance of the elements * * * in the earth.
> 2. The study of the distribution and migration of the individual elements in the various parts of the earth * * * with the object of discovering the principles governing this distribution and migration.

The application of the principles of geochemistry to practical problems in mineral exploration requires the same basic approach. It is built upon the investigation of the average abundance of certain elements in earth materials and of the laws that govern the distribution of elements and the formation of geochemical anomalies. A thorough understanding of geochemical anomalies, how they form, how to find them, and how to appraise them when they are found—that is, an understanding of some of the fundamental laws of geochemistry—is essential in effective geochemical prospecting.

This report is intended primarily as a review of the most important geochemical principles involved in the evolution of geochemical anomalies. A section has also been included on the historical development and application of geochemical methods of prospecting. The data of geochemical prospecting surveys will be reviewed only insofar as they illustrate the principles of geochemical dispersion; detailed information on the results of geochemical prospecting surveys may be found in the reviews cited in Harbaugh (1953) or the literature reviewed. The methods of chemical analysis used in geochemical prospecting are covered in other publications. In this report only incidental reference is made to geochemical methods of exploration for petroleum. A glossary of terms and conversion tables for units of measurement are included at the end of the report.

This report summarizes the results and conclusions of many workers over a period of 20 years. The intent has been to give full acknowledgment by reference to the literature or other notation for all ideas and data that have gone into the preparation of this summary. Many of the concepts, however, have grown out of personal conversations and contacts where the writer may have adopted the ideas of others without realizing the source. In this regard, special mention should be made of the intangible contributions of W. H. Newhouse, T. S. Lovering, L. C. Huff, Helen Cannon, H. W. Lakin, V. P. Sokoloff, F. C. Canney, V. C. Kennedy, J. S. Webb, and J. E. Riddell. The literature used in assembling the data for this report includes only that published before March 1954.

ABUNDANCE OF ELEMENTS IN EARTH MATERIALS

Geochemical anomalies, indicative of commercially important concentrations of elements, can be recognized only by their contrast with unmineralized areas. The normal abundance of an element in any material where the equilibrium has not been upset by the presence of a mineral deposit is commonly referred to as "background." Background values can vary widely owing to natural chemical and physical processes whereby certain elements are enriched and others correspondingly impoverished. For a general guide to the range of background values that may be expected, it is helpful to refer to data that have been compiled on the composition of average igneous rocks, fresh water, and terrestrial plants (table 1). The data on igneous rocks and terrestrial plants have been obtained from published estimates.

The data in table 1 on the major element composition of fresh river water have been taken from estimates by Conway (1942) and Polynov (1937). Estimates for the minor constituents of fresh water have been newly computed from individual published analyses of representative river waters, as summarized in table 2. So far as the writer is competent to judge, only the most reliable data were selected. Because of the wide range in the reported content of many elements in surface waters, the median value as well as the average was computed. As Ahrens (1954) has pointed out, the median of a series of widely scattered values may give a more significant indication of the normal value than the arithmetic mean,

TABLE 1.—*Abundance of some elements in igneous rocks, fresh water, and terrestrial plants*

Element	Igneous rocks [1] (ppm)	Fresh water [2]		Terrestrial plants (ppm) [3]	
		Water (micrograms per liter)	Residue (ppm)	Dry weight	Ash
Aluminum	81,300	700	4,800	20	800
Antimony	1	------	------	------	------
Arsenic	5	1	7	------	------
Barium	250	160	1,100	30	1,200
Beryllium	6	------	------	------	------
Bismuth	.2	------	------	------	------
Boron	3	110	750	5	200
Cadmium	.15	------	------	------	------
Calcium	36,300	29,600	202,700	5,000	200,000
Chromium	200	5.3	36	------	------
Cobalt	23	4.9	33	------	------
Copper	70	20–70	140–480	[4] 5	[4] 200
Fluorine	600–900	250	1,700	------	------
Gallium	15	------	------	------	------
Germanium	7	------	------	------	------
Gold	.005	.0033	.023	------	------
Indium	.1	------	------	------	------
Iron	50,000	510	3,500	------	------
Lead	16	3.4	23	------	------
Lithium	65	------	------	.1	4
Magnesium	20,900	4,400	30,300	700	28,000
Manganese	1,000	52	360	------	------
Mercury	0.077–0.5	.05	.34	------	------
Molybdenum	2.5–15	------	------	.5	20
Nickel	80	15	100	------	------
Niobium	24	------	------	------	------
Platinum	.005	------	------	------	------
Potassium	25,900	2,900	20,200	3,000	120,000
Rare earths	120	------	------	.4	16
Rhenium	.001	------	------	------	------
Rubidium	310	------	------	2	80
Selenium	.09	8	55	------	------
Silicon	277,200	8,000	54,500	1,500	60,000
Silver	.1	.0071	.048	------	------
Sodium	28,300	3,800	26,300	200	8,000
Strontium	300	------	------	20	800
Sulfur	520	5,500	37,900	500	20,000
Tantalum	2.1	------	------	------	------
Tellurium	.0018	------	------	------	------
Thallium	[5] 1.3	------	------	------	------
Tin	40	------	------	------	------
Titanium	4,400	25	170	~2	80
Tungsten	1.5–69	------	------	------	------
Vanadium	150	------	------	.2	8
Zinc	132	~10	~70	[4] 32	[4] 1,300
Zirconium	220	------	------	------	------

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[1] Rankama and Sahama (1950, p. 39–40), except as noted.

[2] For sources, see table 2.

[3] Hutchinson (1943) except as noted; ash computed on basis of 2.5 percent average ash content of terrestrial plants.

[4] Median values of 448 samples collected over unmineralized ground in British Columbia by Warren and others (1952b).

[5] Shaw (1952).

TABLE 2.—*Source data for abundance of elements in fresh water*

Element	Number of samples	Fresh water					Reference
		Water (micrograms per liter)			Residue (ppm) [1]		
		Average (1)	Median [2] (2)	Range [3] (3)	Average (4)	Median (5)	
Aluminum	------	700	----------	----------	4,800	----------	Polynov (1937).
Arsenic	37	1	<3	----------	7	----------	Kehoe and others (1944).
Barium	27	160	120	50–300	1,100	820	Braidech and Emery (1935); Wilska (1952).
Boron	51	110	80	20–150	750	550	Braidech and Emery (1935); Huberty and others (1945).
Calcium	------	29,600	----------	----------	202,700	----------	Conway (1942).
Chromium	24	5.3	2	1–10	36	14	Braidech and Emery (1935).
Cobalt	16	4.9	2.3	.82–10	33	16	Maliuga (1945).
Copper [4]	61	70	30	20–200	480	200	Braidech and Emery (1935); Kehoe and others (1944).
Copper [5]	67	21	5	<2–33	140	34	Huff (1948); Vogt and Rosenqvist (1943).
Fluorine	404	250	200	<100–400	1,700	1,400	U. S. Geological Survey (1952).
Gold	23	.0033	.0014	.0001–.0073	.023	.0096	Haber and Jaenicke (1925).
Iron	172	510	220	40–1,500	3,500	1,500	F. W. Clarke (1924b).
Lead	38	3.4	2	<1–9	23	14	Braidech and Emery (1935); Grushko and Shipitsyn (1948); Huff (1948); Kehoe and others (1940).
Magnesium	------	4,400	----------	----------	30,300	----------	Conway (1942).
Manganese	74	52	10	2–50	360	70	Braidech and Emery (1935); Harvey (1949); Kehoe and others (1944); Wilska (1952).
Mercury	3	.05	.05	.01–.1	.34	.34	Stock and Cucuel (1934).
Nickel	44	15	4	1–13	100	27	Braidech and Emery (1935); Maliuga (1945).
Potassium	------	2,900	----------	----------	20,200	----------	Conway (1942).
Selenium	69	8	1	<1–20	55	7	de Salas (1947).
Silicon	------	8,000	----------	----------	54,500	----------	Conway (1942).
Silver	23	.0071	.0034	<.0001–.01	.048	.023	Haber and Jaenicke (1925).
Sodium	------	3,800	----------	----------	26,300	----------	Conway (1942).
Sulfur	------	5,500	----------	----------	37,900	----------	Do.
Titanium	3	25	~20	----------	170	~140	Kaminskaia (1944).
Zinc	------	----------	~10	----------	----------	~70	Huff (1948).

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[1] Figures for composition of mineral residue of river water are computed from data in columns 1 and 2 on the basis of 146 ppm average salinity for river water (Conway, 1942).

[2] The median (or mode) is statistically the most common value; if all the values quoted are listed in ascending order, the median is in the center of the list.

[3] The figures listed represent the range after the highest and lowest 16 percent of the reported values have been omitted; they are thus analogous to a standard deviation.

[4] Determinations by spectrographic analysis.

[5] Determinations by wet chemical analysis.

inasmuch as the distorting effect of the few excessively high values is eliminated. A measure of the scatter is indicated in column 3 of table 2 by the range of values after the highest and lowest 16 percent have been omitted.

For most elements, the composition of residual and glacial material will not differ greatly from the composition of the rocks from which it was derived, so that the data on average igneous rocks will be a first approximation of the composition of average soils.

DISTRIBUTION AND MIGRATION OF ELEMENTS

The second, and for the purposes of this report the most significant, phase of the science of geochemistry is the study of the laws of equilibrium governing the distribution and migration of elements in the earth. As Clarke (1924a, p. 10) has stated:

> Each rock may be regarded, for present purposes, as a chemical system, in which, by various agencies, chemical changes can be brought about. Every such change implies a disturbance of equilibrium, with the ultimate formation of a new system, which, under the new conditions, is itself stable in turn.

Although Clarke is considering only petrogenesis, his comments apply equally well to processes of weathering, transportation, and sedimentation at the earth's surface.

THE GEOCHEMICAL CYCLE

The disturbance of equilibrium necessary in Clarke's concept of changing chemical systems can be caused by a static change in the temperature and pressure within a closed system or by a dynamic movement of material into new chemical and physical environments. In nature, closed systems are rarely if ever found; virtually all geologic processes involve a certain amount of movement of material.

The movement of earth materials from one environment to another can be conveniently visualized in terms of a partly closed cycle, as illustrated in figure 32. Starting on the right-hand side of the diagram and moving clockwise, sedimentary rocks are progressively metamorphosed as they are subjected to increasing temperature, pressure, and availability of juvenile increments from depths. They may eventually attain a state of fluidity such that on recrystallization they can differentiate into several kinds of igneous rocks and hydrothermal extracts. When erosion brings the resulting suite of rocks into the surficial environment again, the component elements are re-sorted by weathering agencies in accordance with their relative solubility in water. A new series of sedimentary rocks is then deposited and the cycle is closed. The diagram presented as figure 32 is, of course, highly simplified, as in reality large parts of the cycle may be missing in any given case. It is quite normal, for example, for sedimentary sandstone and shale to be exposed to weathering and erosion without remelting or even significant metamorphism.

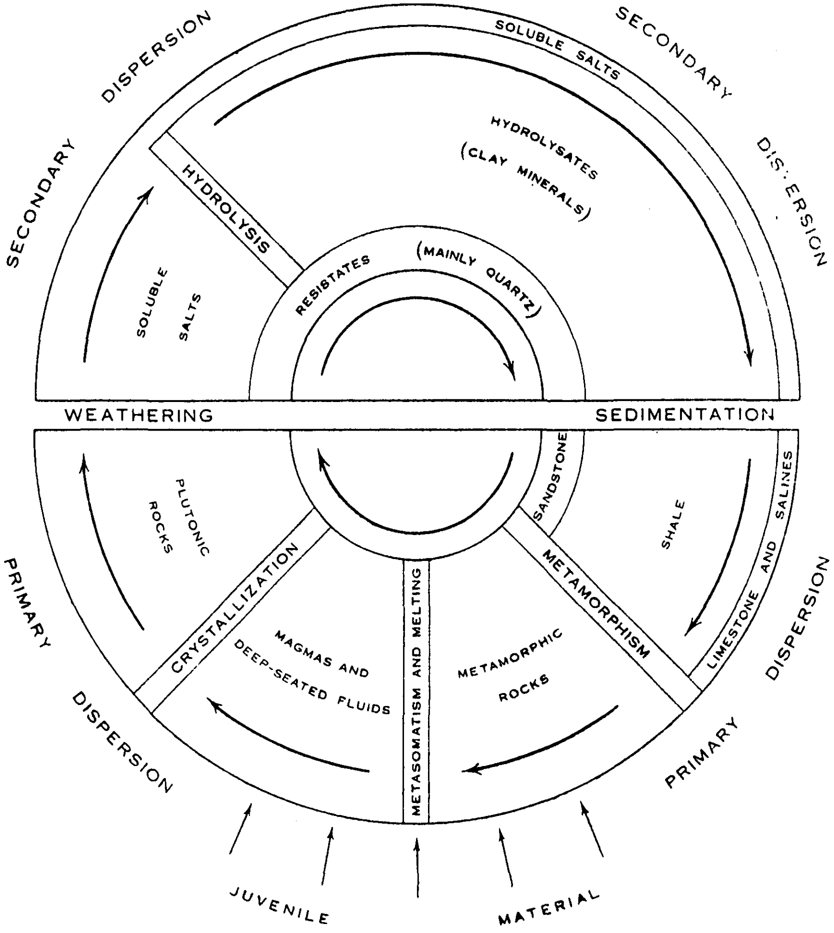

FIGURE 32.—The geochemical cycle.

The geochemical cycle consists of two major parts, one embracing the deep-seated processes of metamorphism and igneous differentiation, and the other the surficial processes of weathering, transportation, and sedimentation at the surface of the earth. The horizontal division in figure 32 indicates the boundary between these two sectors of the geochemical cycle. Petrologists (Holmes, 1928) and some economic geologists (Light, 1953) have referred to deep-seated processes as "endogenetic," and surficial processes as "exogenetic." These terms, although accurately derived and defined, have not been generally adopted outside specialized branches of geology. Economic geologists may refer to ores deposited from upward-moving fluids as "hypogene" and those formed principally by solution and redeposition by surficial solutions as "supergene." These terms also have been accepted only in a specialized sense.

In the previous literature of geochemical prospecting, the two phases have been classified as "primary" and "secondary," respectively. However, the use of these terms leads to some awkward ambiguities. Sedimentary ores can with good reason be called primary, yet they are not of deep-seated origin; also, dispersion of material by hydrothermal solutions from previously formed ore deposits forms a true secondary dispersion pattern that is unrelated to the earth's surface. In this report the somewhat unsatisfactory terms "primary" and "secondary" are used inasmuch as they are perhaps too deeply rooted in the literature to be changed.

The chemical environment of the primary and secondary sectors of the geochemical cycle are entirely different. In the deep-seated environment, temperatures and pressures are high, increasing with depth, and free oxygen is absent; in the surficial environment, temperatures are low, pressures are low and constant, and oxygen is abundant. To this may be added the powerful catalytic effect of organic activity at the surface of the earth, which is absent in the deep-seated environment. Pairs of elements that behave similarly in metamorphic and igneous processes may behave entirely differently when they enter the surficial environment—and vice versa.

DISPERSION PATTERNS

As a result of the movement of earth materials from one chemical environment to another, each element is distributed in patterns that reflect both the abundance of the element in the moving material and the chemical equilibria characteristic of the local environment. In the literature of geochemical prospecting these patterns of distribution have come to be known as dispersion patterns, a term that emphasizes the dynamic processes involved in their formation.

Dispersion patterns may be classified as primary or secondary, depending, respectively, on whether they were formed at depth by igneous and metamorphic processes or at the earth's surface by agents of weathering, erosion, and surficial transportation. Secondary patterns have been further classified as halos, fans, and trains, according to the characteristic shape of the pattern and its geometrical relationship to the ore deposit or other locus of enrichment. A halo is a nearly equidimensional dispersion pattern, enclosing or overlying the source of material. A fan is a pattern spreading outward in one direction from a well-defined source. A train is a linear dispersion pattern formed by movement along drainage channels.

GEOCHEMICAL ANOMALIES

Dispersion patterns in geochemical survey data appear as areas where the abundance of an element is higher than in the surrounding areas. They can be the effect of special features of the environment that cause local enrichments of the element from source material of background composition, or of a source of material containing a higher-than-average amount of the element. If the enriched source is an ore deposit or is related in some way to ore-forming processes, the resulting dispersion pattern may be of material help in mineral exploration, and thus by definition is a geochemical anomaly. One of the principal problems in interpreting the data of geochemical surveys is distinguishing geochemical anomalies from dispersion patterns of no economic significance.

Certain empirical parameters can be worked out that are helpful in identifying and interpreting geochemical anomalies. These involve a consideration of (1) the range of nonsignificant variations in background, (2) the threshold between nonsignificant and anomalous values, (3) the contrast between anomalous and background values, and (4) the homogeneity of the anomalous pattern.

Background range. — Normally, the geochemical data obtained in areas where the equilibrium has not been upset by the presence of a mineral deposit lie statistically within a well-defined range. An example of a background range is presented in column 3 of table 2 for the composition of river water. Geometrical patterns of nonsignificant variations all of which fall within the background range will appear in geochemical survey data and can readily be misinterpreted as geochemical anomalies if their true significance is not recognized. Background variations are somewhat analogous to static in a radio signal or to the "noise" of an electronic amplifier.

Threshold. — If background variations may be compared with noise in an amplifying circuit, the geochemical anomaly is the analogue of the "signal." In interpreting the geochemical pattern of an area containing anomalies, it is usually possible to select a certain limiting cutoff, or "threshold" value below which the variations represent only normal background effects and above which they have significance in terms of possible ore. For example, Warren, Delavault, and Irish (1952b) have reported that in interpreting the copper content of conifer twigs in British Columbia, a value of twice the average background value may be considered "probably anomalous," that is, probably indicative of a mineralized zone lying within reach of the root system of the tree. In their work, the value of twice the average background is the threshold. Similarly, Cannon (1957) has found in the Colorado Plateau area that trees containing more than 1 ppm uranium on an ash basis indicate areas that are probably mineralized. No hard-and-fast rules can be established as to what the threshold value is likely to be in any given area because it will depend on local geochemical factors which are different for different areas. However, it is usually possible to select a threshold contour suitable for the area in question by careful appraisal of the geochemical data from that area.

Threshold, as used in this sense, is not to be confused with the same term sometimes used in analytical chemistry, where it means the limit of detection, or sensitivity, of an analytical method.

Contrast. — Some qualitative measure of the probable significance of an anomalous area is helpful in interpreting geochemical data in terms of probable mineralization. One criterion for significance of an anomaly is the geochemical relief or contrast between anomalous values and background values. This contrast may be expressed as a ratio either of maximum to threshold, maximum to background, or threshold to background, depending on which figure appears to be the most significant. Because of its characteristic response to factors causing enrichment or impoverishment, each element will normally show a different and characteristic degree of contrast with its background. A qualitative idea of the kind of contrast resulting from ore-forming processes can be gained by considering the relative enrichment of elements in ores (table 3). It is reasonable to expect that elements showing a high factor of enrichment in ores will also show a strong contrast in the associated primary anomalies. In secondary anomalies, the contrast for each element will be a complex effect of the enrichment factor in the ore and the factors affecting the mobility of the element in the surficial environment.

A practical example of the importance of contrast in geochemical prospecting was encountered in the Blackbird cobalt district of central Idaho[1]. Here the regional anomalies associated with cobaltite ore show a maximum arsenic and cobalt content of about 1,000 and 300 ppm, respectively, as compared to thresholds of 10 and

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[1] Canney, F. C., and others, 1958, A preliminary report of geochemical investigations in the Blackbird district: U.S. Geol. Survey open-file rept.

30 ppm. The maximum-to-threshold ratio, or contrast, is thus 100 for arsenic and 10 for cobalt, and the anomaly as expressed by the arsenic pattern is statistically more significant than that expressed by cobalt.

TABLE 3.—*Enrichment by ore-forming processes*

Metals	Igneous rocks (ppm) (1)	Workable ore [1] (ppm) (2)	Enrichment factor: ratio (2) to (1) (3)
Principal metals:			
Chromium	200	250,000	1,250
Cobalt	23	5,000	200
Copper	70	10,000	140
Gold	0.005	10	2,000
Iron	50,000	300,000	6
Lead	16	50,000	3,000
Manganese	1,000	250,000	250
Mercury	0.077–0.5	3,000	10,000
Molybdenum	2.5–15	5,000	500
Nickel	80	15,000	190
Silver	0.1	500	5,000
Tin	40	10,000	250
Tungsten	1.5–69	5,000	200
Vanadium	150	25,000	160
Zinc	132	80,000	620
		Maximum content in ore (ppm)	
Byproduct metals:			
Antimony	1	50,000	50,000
Arsenic	5	15,000	5,000
Bismuth	0.2	3,500	17,500
Cadmium	.15	1,000	7,000
Selenium	.09	200	2,000
Tellurium	.0018	24,000	13,000,000

[1] Figures for Cr, Cu, Au, Fe, Pb, Mn, Ni, Ag, Sn, and Zn from Fleischer (1954).

Homogeneity. — The homogeneity of a geochemical anomaly is a measure of the smoothness, or absence of strong local variations, in the distribution of the indicator element. Anomalous areas where smooth geochemical profile curves or contours can be drawn are relatively homogeneous. Anomalies within which values vary erratically through a wide range within short distances may be considered relatively inhomogeneous. The homogeneity of a geochemical anomaly is a prime consideration in establishing the optimum spacing of samples for a geochemical survey.

PRIMARY DISPERSION

Although the same basic principles of physical chemistry apply under all conditions, the processes that dominate the migration of elements in the depths of the earth are very different from the principal processes that are operative under surficial conditions. In a deep-seated environment, geochemical processes are controlled by the relative stability of minerals under any given set of conditions of pressure, temperature, and availability of material. Elements that can enter into the crystal lattice of a stable mineral are immobilized; those that cannot remain in a mobile state until they reach an environment where they can be accommodated in a stable mineral. In a general way, this rule holds true regardless of whether the rock-forming process is regarded as primarily metamorphism, metasomatism, or crystallization from a magma.

The effect of availability of material is such that most minerals are stable only in the presence of an abundant supply of the component elements. The common rock-forming minerals, therefore, are those containing only the nine most common elements as major constituents. These elements are, in order of decreasing abundance, oxygen, silicon, aluminum, iron, calcium, sodium, potassium, magnesium, and titanium. In terms of atomic abundance, hydrogen is also a major constituent of rocks, although its relative abundance is difficult to estimate in quantitative terms. Rare elements occur as major constituents only in a few accessory minerals of igneous and metamorphic rocks, principally zircon (zirconium), and monazite (rare earths, phosphorus). Thus out of the 88 naturally occurring elements, only 12 plus the rare earths occur as major constituents in common rock-forming minerals.

Many of the remaining elements can be partly incorporated into one or more of the common minerals by occupying a position in the crystal lattice that is ordinarily filled by one of the major component elements. This can take place only when the physical properties of the substituting ion are within certain limits of those of the ion for which it is proxying. For example, the ionic radius and ionization potential of lead are close to those of potassium, and therefore lead can substitute for potassium in potash feldspars. Similarly, zinc, copper, and cobalt can proxy for iron and magnesium in amphiboles and biotite, and fluorine can proxy for hydroxyl in micas. It is generally assumed that the abundance of rare elements in minerals of this kind is proportional to their relative abundance in the material from which the crystals were formed. Other factors being constant, therefore, a tin-rich mica from a pegmatite dike implies a tin-rich pegmatitic fluid.

The constituents that cannot be accommodated in the lattice structures of rock-forming minerals remain behind and are concentrated in the mobile residual fluid. A very small part may be mechanically trapped either within the lattice or as minute films between the crystal interfaces. The bulk of it, however, goes out of the system. The progressive enrichment of rare elements in the residual fluid makes possible the formation of minerals containing rare elements as major constituents and accounts for the assemblage of unusual minerals found in pegmatite and greisen. Water, which cannot be entirely accommodated in the high-temperature minerals, is continuously enriched in the residual fluids. With decreasing temperature, the water-rich residual fluids begin to assume the familiar properties of aqueous solutions. The hydrothermal vein deposits that comprise most of our base-metal sulfide deposits are generally believed to be precipitated at this stage in the primary geochemical cycle. Eventually the residual fluids reach the surface of the earth where they may either blend with the ground water or come to the surface as springs.

Primary dispersion patterns, properly speaking, include the end products of all the processes of metamorphism, metasomatism, and magmatic differentiation outlined above. All phases of the process are closely interrelated, and the chemical equilibria at one stage will predetermine to a great extent the course of the process at later stages. When the predetermining conditions are favorable, ore bodies will be formed. At the same time, the formation of ore bodies predetermines the processes and products of later fractionation. These equilibria may be reflected in easily measured chemical characteristics of primary dispersion patterns that are formed before, during, or after ore deposition.

Three kinds of primary dispersion patterns, or primary anomalies, are of particular importance in ore finding: the geochemical province, within which the chemical composition of rocks can be correlated with the occurrence of certain kinds of ore; dispersion patterns formed by the movement of aqueous fluids at the time of ore deposition; and dispersion patterns produced by movement of gases at low temperatures.

GEOCHEMICAL PROVINCES

A geochemical province, for these purposes, may be defined as a segment of the earth's crust in which the chemical composition is significantly different from the average. Evidence for the existence of a geochemical province is commonly sought by studying comparisons in the composition of igneous rocks.

In working with the major-element content of igneous rocks, normal processes of petrogenesis may cause variations that mask the pattern due to fundamental differences in the composition of the parent magmas or other deep-seated fluids. A variation in the minor-element composition of igneous rocks that are otherwise similar, however, may provide reliable criteria for distinguishing a true geochemical province. Here it may be presumed that igneous rocks of similar major-element composition are the results of similar processes of petrogenesis but that the contrasts in minor-element composition reflect an original difference in the composition of the primary materials out of which the igneous rock was formed. Thus, if an area is found where all diabase intrusions contain four times as much titanium as similar intrusions outside the area, it is probable that the diabase magma was enriched in titanium. The area may then be considered a titanium-rich province, at least as far as the composition of diabase is concerned.

Metallogenic provinces, or areas characterized by an unusual abundance of ores of a particular metal, have long been recognized by economic geologists. Examples are cited of the copper-producing areas of the southwestern United States, and of the gold fields of the South African Witwatersrand (Bateman, 1950, p. 319-325). These classic examples of metallogenic provinces are defined largely or entirely on the basis of production figures. As more data are gathered it is becoming apparent that at least some metallogenic provinces coincide with areas where the igneous rocks are also enriched in the same metals; that is, an abundance of ores of a certain kind is simply one manifestation of a geochemical province.

Tin is an element that enters into the crystal lattice of the common igneous minerals only to a very limited extent, with the result that if abnormally large amounts of tin are available in the fluids that form the igneous rocks it will be enriched in the residual juices from which it may be precipitated late in the igneous cycle as hydrothermal cassiterite. At the same time the abundance of tin available in the primary igneous environment will be reflected by a higher-than-normal tin content of certain minerals of igneous rocks.

A relationship of this kind has been reported by Ahrens and Liebenberg (1950) from South-West Africa, where the mica of pegmatite dikes near tin veins contains from 10 to 100 times as much tin as mica from similar dikes in areas where no tin mineralization is known. A somewhat similar relationship has been reported from the tin fields of Malaya and Indochina, where Goloubinoff (1937) has reported from 100 to 2,500 ppm tin in late igneous differentiates from this area as compared with 40 ppm for average igneous rocks.

The same writer also reports that a suite of igneous rocks, including pegmatite, norite, and diabase, collected from gold-bearing districts contain from 8 to 25 times as much gold as equivalent rocks from barren areas. A similar correlation between the nickel content of ferromagnesian minerals in basic igneous rocks and the tenor of nickel in associated pyrrhotite ores has been pointed out by J. H. L. Vogt (1923).

Igneous rocks and hydrothermal extracts that are associated in space but formed at widely separated times may be enriched in the same suite of elements. For example, in northern Nigeria where a niobium-thorium province has been described not only igneous rocks of the post-Cretaceous alkaline complex but also pegmatite dikes of probable Precambrian age all contain niobium and thorium minerals in noteworthy quantities (Davidson, 1951). Similarly, a boron province in southern California is indicated by the coincidence of tourmaline-rich pegmatites, recent saline deposits, and modern borate-rich thermal waters.

To the prospector, geochemical provinces may be useful as preliminary guides in his selection of areas for more detailed search. It has long been a maxim in the exploration business that "if you are looking for elephants, go to elephant country." This could be paraphrased in geochemical language to read: "If you are looking for deposits of a certain element, go to a geochemical or metallogenic province that is enriched in that element." The traditional prospector identifies his province on the basis of previous mineral discoveries. This is effective, of course, only where earlier prospecting activity has uncovered enough mineral occurrences to attract attention. Many areas of the earth, however, are either so remote or so heavily covered by overburden that no preliminary prospecting of any kind has been possible. In such areas it would be most helpful to have some simple means of selecting promising areas. The evidence to date indicates that under favorable conditions it may be possible to select favorable areas by trace analysis of relatively few samples of igneous rocks or minerals and by interpretation of the data in terms of metallogenic provinces.

DISPERSION IN AQUEOUS FLUIDS

Most mineral deposits are the result of deposition of material from an aqueous fluid of some kind moving through a system of channels in the rock. The exact nature of the fluid from which the ore is precipitated may be very different for different kinds of mineralization. Under some conditions it may be an aqueous solution at relatively low temperatures; under others a water-rich gaseous or supercritical fluid or even an aqueous magma. The nature of the ore-forming fluid is a subject of very active investigation and debate at the present time.

As the aqueous fluid passes along its system of channels, its physical and chemical environment is constantly changing; chemical reactions take place within the fluid and between the fluid and the wall rock of the channel in an effort to maintain equilibrium with the environment. The most conspicuous of these reactions, or at least the most important economically, is the creation of ore minerals and their deposition as an ore deposit.

Alteration patterns, where the effect of the mineralizing solution is primarily the modification of the original mineral assemblage, have been the subject of active investigation by economic geologists for many years, and their importance in ore finding is well established. Alteration studies are based on mapping the distribution of diagnostic secondary minerals that can be identified directly either in hand specimen or under the microscope. Patterns of hydrothermally dispersed metals, however, normally cannot be mapped without chemical analyses of the altered material. With the recent application of rapid analytical techniques to the study of hydrothermally modified rock, the importance of hydrothermal dispersion patterns of metals is being recognized as an aid both in explaining the genesis of ore deposits and in prospecting for them.

In considering the characteristics of the dispersion patterns and particularly the geochemical anomalies that are formed by hydrothermal and pneumatolytic transportation of material, the character of the fluid is perhaps not as important as the geometry of the channels through which it flows, or the "plumbing" of the mineralizing system. On a geometrical basis, dispersion patterns in channels can be conveniently classified as (1) areal patterns, resulting from widespread impregnation of a large mass of rock by hydrothermal solutions or other fluids emanating from depth, (2) "leakage" patterns within a well-defined system of solution channels and (3) wall-rock patterns, where the minor-element composition of the rock adjoining the solution channels has been modified by hydrothermal activity.

Areal patterns.— Areal patterns of dispersed metal may enclose groups of deposits and thereby serve to define the boundary of the area in which ore is likely to occur.

Gross (1950, 1952) in studying the relation of gold mineralization to granitic stocks in western Ontario found increasing radioactivity of granite in the direction of the mineralized area. Chemical studies showed that with the increasing radioactivity there was an increasing content of uranium, thorium, zirconium, silicon, and heavy metals in the granite. He postulates that these elements were all concentrated by movement of igneous extracts in the direction of easiest release of pressure. The same pressure factor may have controlled the localization of the gold ore.

An areal pattern of perhaps somewhat different origin was observed in the Blackbird cobalt district of central Idaho.[2] Analysis of soil samples collected at 100-foot intervals along traverses covering a total area of about 8 square miles outlined an area at least 3 miles long and as much as 1 mile wide where the average cobalt content is about 100 ppm as compared with a background of about 10 ppm. The threshold for the cobalt-rich area is 35 ppm. Within the cobalt-rich area, the principal cobalt mineral in all the known sulfide deposits is cobaltite, whereas outside the area the principal cobalt mineral in all but one deposit is cobaltiferous arsenopyrite, which is of no commercial value. Thus, the only likely place to look for cobaltite deposits is within the area of cobalt-rich soils. Although the mode of occurrence of the cobalt in the parent rock from which the cobalt-rich residual soil was derived is not known, a dissemination of hydrothermally deposited cobalt minerals in an intricate lacework of mineralized fractures would not be inconsistent with the evidence.

Kimura, Fujiwara, and Yasudo (1950) describe altered volcanic rocks near the Sado gold mine in Japan in which the copper and silver content apparently is an indication of gold-copper mineralization. Particularly, they report a high silver-copper ratio in the rocks near some of the mines.

Leakage.—Patterns of metal dispersed in the rocks and in fracture zones over blind ore deposits have been mapped in a number of areas. Dispersion patterns of this kind have been called "leakage halos," following the concept that some of the metal has "leaked" upward from the ore deposit. It is presumed, but by no means proved, that leakage halos represent the spoor of nearly spent mineralizing fluids moving upward after the major part of their metallic load has been left behind. The evidence could be applied equally well to downward-moving solutions that have not yet reached the site of deposition.

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[2] See footnote 1 on p. 234.

Perhaps the best example of a leakage halo over blind ore is that reported by Lovering, Sokoloff, and Morris (1948) in the Tintic district of Utah. In that area complex lead-zinc-silver ore occurs in limestone of Paleozoic age overlain by preore, but barren, rhyolite. Surface studies of the rhyolite over known ore have disclosed areas of argillic and pyritic alteration that include the up-rake projections of the underlying ore. The alteration halos, however, cover so large an area as compared with the ore bodies that they are of limited use in guiding diamond-drill exploration. Sampling and chemical analysis of the altered rhyolite, however, disclosed a heavy-metal anomaly that coincides closely with the up-rake projections of one of the principal ore shoots. The writers suggest that this anomaly corresponds to the surface trace of the channels through which the nearly spent mineralizing solutions escaped. Even though the rhyolite was not a favorable host for ore deposition, enough metal was deposited along the solution channels to be detectable by trace analysis.

Another example of a leakage halo was reported by Kennedy[3] in his studies of the rocks overlying zinc ore in the Shullsburg district of southwestern Wisconsin. Analysis of cores from four drill holes, penetrating ore contained in a sequence of flat-lying sedimentary rocks, showed high zinc values extending 58, 108, 128+, and 138+ feet, respectively, into the rocks overlying the ore. In the same holes, high iron values extended upwards for 103, 108, 128+, and 138+ feet. The somewhat erratic variations observed in the anomalous values over ore are interpreted as evidence that the halo was accounted for more by small veinlets than by a homogeneous diffusion of metals. Kennedy concluded that weathering of the zinc-rich rocks comprising the leakage halo might produce zinc-rich soils and that prospecting for ore buried 50 to 100 feet below the surface might be possible by soil analysis.

At Johnson Camp near Willcox, Ariz., Cooper and Huff (1951) have described a leakage halo in the fractured rock 600 feet above the concealed Moore ore body. The ore is localized in one bed of a moderately dipping sequence of partly silicated calcareous rocks. Chip samples of rock collected at close intervals across outcrop surfaces were composited in sections of 50 feet or more. The heavy-metal content of samples collected in this manner along a series of profile lines showed an anomalous area similar in shape to the horizontal projection of the ore deposit, but displaced about 200 feet to one side.

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[3] Kennedy, V. C., 1949, Mineralization surrounding ore in the southwestern Wisconsin lead-zinc district: Pa. State College, unpublished thesis.

At the Amulet deposit near Noranda, Quebec, Riddell (1950) analyzed rock samples for heavy metal that could be extracted in cold acid. He outlined an area of high-metal content in the rock directly overlying two flat-dipping ore bodies. His threshold was 9 ppm of extractable metal, compared with a background of about 2 ppm. An alteration halo is also associated with the ore, but is not related in any simple way to the geochemical anomaly and is thought to be preore.

The above examples of leakage halos are taken from studies of the essentially unweathered rock. In each example, the traces of metal were presumably distributed throughout fairly large masses of rock in intricate fracture systems, some of which were visible, as at Johnson Camp, but most of which were either so fine or had been resealed so tightly that they were not obvious on casual inspection. Also, each of these examples of leakage halos shows a pattern crosscutting the depositional structure of the overlying rocks.

Another variety of leakage halo is in barren veins and fissure zones over ore shoots, where presumably the ore-forming fluids moved upward along the vein or fissure system. Here the leakage halo occurs only within the limits of a well-defined planar structure, rather than being dispersed throughout a large volume of rock. For example, in the Parral district of Mexico, Schmitt (1939) reports that the distribution of silver in noncommercial veins can be used as an indication of an ore shoot at depth. In the Santa Rita district of New Mexico, Graf and Kerr (1950) found lead anomalies in Tertiary fault zones that could be correlated with ore bodies in the underlying pre-Tertiary rocks.

Leakage halos have also been mapped by analyzing soil or vegetation over the geochemical anomaly in the immediately underlying bedrock. Kennedy (1956) and Cooper and Huff (1951) mapped soil anomalies that corresponded with observed leakage halos in the bedrock. White and Allen (1954) found a copper anomaly in glacial soil 75 feet above the top of a blind ore body in the Boundary district of British Columbia. In the Austinville zinc district of Virginia, Fulton (1950) mapped zinc anomalies in soils along the trace of preore faults that intersect the zinc ore at depth.

Wall-rock dispersion. — Several examples have been described where traces of the ore metals are dispersed into the wall rock of the ore body. Most of these dispersion patterns were undoubtedly formed at the time the ore bodies were being deposited, when juvenile mineralizing fluids provided a ready source of metals. A few, however, may be the effect of later hydrothermal solutions entering a preexisting ore deposit and remobilizing the constituent elements.

In the East Tintic district of Utah, Morris (1952) describes a wall-rock halo where the copper, lead, and zinc content of the limestone country rock decays logarithmically from a maximum value next to the ore, to background within a distance of 5 to 20 feet. The logarithmic shape of the decay curve and the fact that the curves for each of the three metals are different are interpreted as evidence that the metals moved by a process of ionic diffusion through a static solvent contained in the pore spaces of the rock.

Graf and Kerr (1950), working at Santa Rita, N. M., found wall-rock halos of lead and zinc in fractured limestone adjoining lead-zinc deposits, with the maximum zinc content close to the ore and the maximum lead content farther away. They conclude that the metal was introduced through systems of small fractures, inasmuch as they found only negligible dispersion into unfractured wall rock.

H. D. B. Wilson (1944) at Goldfield, Nev., reports a complex pattern of leaching and enrichment of many of the common elements in the wall rock of gold veins, but no well-defined pattern of dispersion of the minor elements.

Stoll (1945), in studying the minor-element content of the wall rocks of New England pegmatite deposits, found increased concentrations of beryllium. He postulates that the beryllium was added to the wall rock by solutions emanating laterally from the main channels through which the pegmatitic liquids were flowing.

Mitcham (1952) describes envelopes of "indicator" minerals, particularly arsenopyrite and hydrothermal chlorite around ore shoots in the Coeur d'Alene district of Idaho.

Applications. — Each of the various kinds of primary anomalies formed by the movement of aqueous fluids has its particular sphere of usefulness in prospecting. Areal patterns will probably be most useful in reconnaissance exploration for mineralized districts. Leakage halos are outstanding in that they are one of the few available indicators of deep ore bodies that do not come to the surface of bedrock. Wall-rock halos are likely to be most useful in underground exploration, where it would be helpful to know whether or not the end of a crosscut or drill hole is within a short distance of ore. Morris (1952), in fact, describes an example of a crosscut ending in limestone where the metal content was well above background; later extension of the crosscut broke into a new ore body within 10 feet.

GASEOUS DISPERSION

A few of the components of the earth's crust move at low temperatures as gases through the pore spaces of rocks and soils from which they escape directly into the atmosphere. Movement of this kind depends on the existence of continuous open channels through which the gas can move without hindrance. Near the surface the flow of gas may be modified by changes in barometric pressure, causing alternating inward and outward movement or "breathing."

Gaseous dispersion patterns may be detected either by direct analysis of the gas itself, or under some conditions by analyzing the material through which the gas has passed for products of condensation.

It is claimed that volatile hydrocarbons may escape from oil reservoirs through the overlying rocks and pass by way of the soil into the air. This possibility is the basis for many of the geochemical methods of exploration for petroleum, where soil or soil air is systematically sampled and analyzed for traces of certain diagnostic hydrocarbon compounds. Hydrocarbon anomalies may be thought of as very weak oil seeps, so weak that the deposition of material at the surface cannot be recognized without chemical analysis. Although geochemical methods of locating petroleum are the subject of a very extensive literature, their general effectiveness is a matter of considerable difference of opinion among oil men. A full discussion of these problems is beyond the scope of this report.

The nuclear decay of certain radioactive elements results in the generation of noble gases. Radon and helium are produced from the disintegration of uranium, and thoron and helium from thorium. Similarly, argon is produced by the decay of the K^{40} isotope of potassium. Under favorable conditions these may travel substantial distances from the source to form patterns that are helpful in prospecting for the parent elements. Arndt and Kuroda (1953) found a significant radon content of stream waters draining the uraniferous black shale beds of Arkansas. They also report a high radon content of spring water emanating from a uranium-bearing syenite. Inasmuch as the noble gases are chemically unreactive, they cannot have any chemical effect on the matrix through which they travel and tend to escape into the atmosphere by the shortest possible route. It has been estimated that radioactive spring water loses 41 percent of its radon to the atmosphere in the first 4 feet of surface flow. Radon and thoron, however, decay through a series of intermediate radioactive products including isotopes of polonium, lead, and bismuth. Conceivably dispersion patterns formed by the radioactive daughter products of radon and thoron could be detected and measured by systematic studies of soils and waters.

Of the nonradioactive ore metals, mercury is the only one whose gaseous dispersion patterns have been given any serious thought as an aid in prospecting. At the Khpek mercury mine in Russia, Saukov (1946) describes a zone of mercury-rich shale and sandstone 2,000 meters wide embracing all the known occurrences of mercury in that vicinity. From a consideration of the vapor pressure of mercury occurring in mercury minerals, he interprets the pattern as the effect of gaseous dispersion of mercury from the primary deposits into the porous country rock.

Like leakage halos, the patterns formed by gaseous dispersion can provide an indication of buried ore that does not come to the surface of bedrock. Its usefulness in prospecting, however, is limited to the very few materials that are either volatile or that give off a volatile product, particularly petroleum, mercury, and uranium.

MOBILITY OF ELEMENTS IN THE SURFICIAL ENVIRONMENT

The physical and chemical environment of the earth's surface differs in almost every respect from that prevailing at depth where igneous and metamorphic rocks with their associated mineral deposits are formed. Minerals that are stable under deep-seated conditions are decomposed in the new environment, and a new suite of stable materials is formed. A complex series of new physical, chemical, and biological equilibria arises, beginning with the initial disintegration of the primary rocks and ending ultimately with the deposition of a fresh sequence of sedimentary rocks.

A radical change in the habits of movement of the elements results from this change in the physical and chemical environment. The factors affecting the relative mobility of elements under deep-seated conditions are no longer operative, and the scene is dominated by a completely new set of influences. A few elements, such as cobalt, that were originally immobilized by incorporation into high-temperature minerals, become relatively mobile under surficial conditions; for a few others, such as silicon, the reverse relationship holds. In general, there is no immediately obvious correlation between the mobility of elements in the primary and in the secondary geochemical cycles.

The mobility of elements in the surficial environment and the factors governing it are of particular importance in geochemical prospecting. The characteristic behavior of elements released by the weathering of mineral deposits determines the nature of the resulting dispersion patterns and geochemical anomalies. An understanding of the principles controlling mobility is necessary if the geochemical surveys are to be planned intelligently and the resulting anomalies interpreted accurately.

Mobility, or the ease and speed with which material moves, is the resultant of a vast complex of physical, chemical, and biological factors. The most important of these factors will be reviewed. Inasmuch as the net effect of all these factors acting at once cannot be computed on a quantitative basis, some empirical estimates of the relative mobility of the important elements in the surficial environment will be given.

PHYSICAL FACTORS AFFECTING MOBILITY

Gravity is the dominant force causing nongaseous material to move on the surface of the earth. Gravity, however, is opposed by the forces of friction, which must be overcome before movement can take place. In solid dry aggregates, the frictional force is high, but with the addition of moisture the system may become lubricated to a point where movement can begin. Depending on the composition and structure of the solid aggregate, movement takes the form of landslides, slumping, mudflows, or other commonly observed phenomena. Where the material moving under the influence of gravity is largely aqueous, the frictional force arises out of surface attraction and drag against the solid sides of the channel. In a rock where the moisture is held in minute fractures, the effect of gravity may be negligible compared with the forces tending to hold the water molecules in place. In a moderately permeable soil, the gravity movement is slow but measurable. In the open channels of streams and rivers gravity flow is relatively free, and movement for great distances can take place in a relatively short time.

These elementary considerations lead to a conclusion of prime importance in evaluating the mobility of elements in the surficial environment: inasmuch as water can move more freely than any other material on the earth's surface, an equivalent mobility is imparted to anything carried by the water. Materials that travel in solution or colloidal suspension in the water have the highest mobility. Material occurring as fragments swept along or lubricated by water have a lower mobility. Materials that are moved by water only rarely have the lowest mobility. Mobility, therefore, is almost synonymous with the tendency of a material to be stable in aqueous solutions or suspensions.

In addition to gravity and the forces impeding its action, some other physical forces play an important role in the movement of material under some conditions. Capillarity can move solutions through the fine pore spaces of soils against the force of gravity. If moisture is removed from the upper part of the capillary fringe by evaporation or plant growth, a substantial volume of water can be moved by capillary forces.

Diffusion through a static aqueous system can move ions in the direction of decreasing ion concentration. In a fine-grained crystalline matrix, ions can also move along the surface of mineral particles and migrate from one particle to another even when the pore spaces between particles are empty.

The action of ice and frost as a transporting agent will be reviewed in later sections. The action of wind is of little economic importance in the dispersion of the weathering products of ore bodies.

CHEMICAL FACTORS AFFECTING MOBILITY

It has been shown how water responding to the force of gravity is the dominant agent of physical transport on the earth's surface. Anything that can be carried by water is mobile, and material that cannot is relatively immobile. Water also dominates all chemical reactions in the surficial environment. It is the solvent within which virtually all the chemical reactions on the surface of the earth take place. Without water the effect of oxygen and carbon dioxide would be negligible, and biological processes would be impossible.

The unique catalytic effect that water has on chemical reactions stems from its capacity to dissociate soluble inorganic compounds into their component ions; that is, to break some of the bonds holding the compounds together. All chemical changes involve the breaking of bonds. At elevated temperatures, bonds are broken by thermal agitation of the atoms within the molecule, and chemical reactions can then proceed quickly to equilibrium. At atmospheric temperatures, however, broken bonds can exist and reactions proceed only under the influence of a powerful catalytic agent such as water.

Because of the dominant importance of water as a catalyst in all chemical reactions at the surface of the earth, some of the properties of aqueous solutions should be reviewed. The properties of ionic solutions of most importance in understanding the formation of secondary geochemical anomalies are hydrogen-ion concentration, solubility of salts, coprecipitation, sorption, oxidation potential, and the formation of complex ions and organic compounds.

Hydrogen-ion concentration. — The relative acidity or alkalinity of an aqueous solution may be quantitatively expressed in terms of the concentration of hydrogen or hydroxyl ions in solution. Pure water under standard conditions is neutral; that is, it has an equal concentration (10^{-7} moles per liter) of both hydrogen and hydroxyl ions. A 1 *N* acid contains approximately 1 mole per liter of hydrogen ions, and by virtue of the dissociation constant of water contains at the same time 10^{-14} moles of hydroxyl ions; the reverse holds for a 1 *N* solution of a base. It is customary to express acidity in terms of the negative logarithm of the hydrogen-ion concentration; a value known as the pH. Thus under idealized conditions a neutral solution has a pH of 7.0, a 1 *N* acid has a pH of 0, and a 1 *N* base, 14.

The pH of a solution may be measured quantitatively by determining the electrical potential developed between a special electrically conducting glass electrode and a reference electrode when both are immersed in the same solution. Portable pH meters employing this principle are best suited for the measurement of the pH of natural waters. The pH may also be measured by means of colored indicator reagents, marketed either as solutions or as impregnated papers. Colorimetric pH determinations, however, apparently cannot be depended upon for weakly buffered natural waters.

The pH of a soil is defined as the pH of an aqueous mud prepared by adding distilled water to the soil (Lepper, 1950, p. 44). A similar measurement can be made for pure minerals by pulverizing the mineral grains in pure water and testing the pH of the resulting suspension (Stevens and Carron, 1948).

The normal pH of surface waters ranges from about 4.5 to 8.5, and most of the chemical reactions in the weathering cycle take place within this range. The outstanding exception to this rule is the oxidation of pyrite and marcasite, where the free sulfuric acid formed creates local conditions of extreme acidity. The normal range of pH for soils lies between 4.0 and 9.0.

The solubility of most elements and the stability of their compounds is extremely sensitive to the pH of the aqueous environment. Only a few elements, among which are the alkali metals (such as sodium and potassium), and some of the elements forming acid radicals (such as nitrate and chloride), are normally soluble as dissociated ions throughout the pH range. Most metallic elements are soluble as cations in acid solutions but tend to be precipitated as hydroxides or basic salts with increasing pH. Table 4 gives the general order in which ions of some of the important metals begin to be precipitated from aqueous solutions as the pH is increased. As the pH is further increased some of these again become soluble as complex anions, such as the zincate, aluminate, and chromate radicals. Some other elements, notably silicon, are soluble in water only as complex anions in alkaline solutions. The simple relationships described above apply only in the absence of ions that form insoluble precipitates or soluble complex ions with any of the other components of the system. The figures given in table 4, therefore, indicate only trends and tendencies; in natural solutions of a wide diversity of composition, marked deviations from these rules may be noted on occasion.

TABLE 4.—*pH of hydrolysis of metals from aqueous solutions as hydroxide or basic salt*

[From Britton (1942, v. 2, p. 79); the concentration of metal salts in the solutions used falls within the range from 0.025 M to 0.0025 M]

Element	pH	Element	pH	Element	pH
Magnesium	10.5	Cobalt	6.8	Aluminum	4.1
Silver	7.5–8.0	Yttrium	6.8	Mercurous	3
Manganous	8.5–8.8	Cadmium	6.7	Thorium	3.5
Lanthanum	8.4	Nickel	6.7	Indium	3.4
Cerous	7.4	Lead	6.0	Ceric	2.7
Mercuric (Cl)	7.3	Beryllium	5.7	Mercuric (NO_3)	2
Praseodymium	7.1	Ferrous	5.5	Stannous	2
Neodymium	7.0	Cupric	5.3	Zirconium	2
Zinc	7.0	Chromium	5.3	Ferric	2
Samarium	6.8	Uranic	4.2		

The strong acids evolved by the oxidation of pyrite or marcasite not only have a strong corrosive effect on other ore minerals and on the wall rocks but also can stabilize most of the ore metals as simple soluble cations. As the acidity of these solutions is reduced by chemical reactions and by dilution, the metals tend to precipitate in the order of increasing pH of hydrolysis, as shown in table 4.

In normal soils, the pH of the soil has a profound effect on the rate at which the components are either leached or accumulated. This relationship has been the subject of intensive study by agricultural scientists, who are concerned with the availability of mineral nutrients to crops. Availability of an element is a function of its solubility, which in turn is related to pH. In some experiments it has been found that optimum availability of a nutrient element occurs in a soil where the pH is near the pH of hydrolysis. In the acid range where the element is readily soluble, leaching may have reduced the content of the element below a healthy nutrient status;

in the range where the element has been rendered insoluble by hydrolysis, the available fraction may also be too low.

A few of the experimental results of agricultural research might profitably be compared with the idealized data of table 4. Trenel (1946) reports that a soil pH below 5 causes the solubility of toxic aluminum. Knowles (1945) finds that adding lime to a soil increases the pH from 6.2 to 7.3 and reduces the content of exchangeable (soluble) zinc by a factor of 30. Lott (1938) reports that the upper pH limit of zinc toxicity in his soils is 6.0. Peech (1941) observed that only a very small fraction of the exchangeable copper in soils could be removed by leaching with solutions of pH 6 and above; the same effect for zinc was observed at pH 7.5, and for manganese at pH 7. Lucas (1948) conducted experiments that indicated a precipitation of copper hydroxide in soils where the pH is greater than 4.7.

Throughout these experiments with soils, the limiting pH of solubility of the metals in natural solutions obviously departs somewhat from the values quoted in table 4, which are based on experimental solutions of known composition. The values illustrate the intimate relationship existing in nature between solubility and the pH of the solution, however.

Solubility of salts. — The ability of an ion to remain in an aqueous solution is limited by the solubility of the salts it forms with ions of opposite charge present in the same solution. The precipitating effect of the hydroxyl ion has already been discussed in considering the pH of solutions. Other anions commonly present in natural solutions are carbonate, chloride, and sulfate. The metal content of saturated aqueous solutions of some salts that occur in nature as secondary minerals is given in table 5.

In dealing with laboratory solutions of known composition it is helpful to visualize the solubility of an inorganic precipitate in terms of a function known as the solubility product. At a specified temperature and pressure, the solubility product is equal to $[M]^x[N]^y$ where $[M]$ and $[N]$ are the ion concentrations in moles per liter in a saturated solution of the solid M^xN^y. For example, the solubility product of CaF_2 (fluorite) is $[Ca^{++}]$ $[F^{-2}]$ and is numerically equal to 3.9×10^{-11}. The solubility product rule tells us that a salt may be precipitated from a saturated solution by increasing the concentration of any of the participating ions. Conversely, a salt can dissolve in any solution where the product of the concentrations of the common ions is numerically less than the solubility product constant.

Except as noted, the data of table 5 are for solubility in water at a pH of 7. The solubilities of the salts of weak acids, such as fluorides, carbonates, and phosphates, commonly increase with decreasing pH. Also, the amount of carbon dioxide dissolved in the water will modify the solubility of carbonates. Because of the wide variations in the pH and carbon dioxide content of natural waters, absolute values for solubility cannot be assigned. The data of table 5 are intended only to give a qualitative idea of the general order of magnitude of mineral solubilities.

TABLE 5.—*Solubility of salts occurring in nature as secondary minerals*

Salt	Equivalent mineral	Composition of saturated aqueous solution [1] (ppm)	Temperature (°C)
$AgCl$	Cerargyrite	Ag^+ 1.46	25
$BaSO_4$	Barite	Ba^{+2} 1.3	25
CaF_2	Fluorite	F^- 8	18
$CaSO_4 \cdot 2H_2O$	Gypsum	SO_4^{-2} 1140	18
$CuCO_3 \cdot Cu(OH)_2$	Malachite	Cu^{+2} [2] 12	20
$2CuCO_3 \cdot Cu(OH)_2$	Azurite	Cu^{+2} [3] 7	20
$PbCO_3$	Cerussite	Pb^{+2} 1.3	18
$PbSO_4$	Anglesite	Pb^{+2} 27	18
$Pb_5Cl(PO_4)_3$	Pyromorphite	Pb^{+2} [4] .03	37.5
$ZnCO_3$	Smithsonite	Zn^{+2} 107	18

[1] Unless otherwise specified, figures are for solubility in pure neutral water taken from data assembled by Seidell (1940).

[2] In presence of 0.29 g CO_2 per liter.

[3] In presence of 0.34 g CO_2 per liter.

[4] Computed from solubility product value of $10^{-79.115}$ determined by Jowett and Price (1932). At pH 5.0, solubility of pyromorphite is 0.6 ppm.

In nature, the formation of most of the minerals listed in table 5 appears to be limited to very special environmental conditions where high concentrations of the reacting ions are being introduced into the system from a local enriched source. Outstanding among these special conditions is the environment of an oxidizing sulfide deposit. The local abundance of both lead and sulfate ions produced by the oxidation of galena and other sulfide minerals very commonly exceeds the solubility product of lead sulfate, with the ensuing formation of anglesite. Cerargyrite forms by the reaction of abundant silver ions with the chloride naturally present in ground waters; gypsum precipitates where abundant sulfate reacts with the lime dissolved in normal waters. Similarly, smithsonite, witherite, copper carbonates, wulfenite, and many other minerals are precipitated from aqueous solutions near the site of oxidizing sulfide minerals, where the concentrations of the component ions is relatively high. Minerals of this kind will not be formed, of course, if the precipitates take the form of colloidal dispersions that are removed with the circulating ground water, as is commonly observed with the precipitation of iron oxide and silica (Moore and Maynard, 1929).

The breakdown of simple compounds in the surficial environment is also governed by the abundance of component ions in the solvent solution. Many secondary minerals that are stable in the presence of the acid, metal-rich, and sulfate-rich solutions characteristic of the environment of an oxidizing sulfide deposit redissolve when they come in contact with normal solutions. Secondary zinc minerals can survive only when they are fairly close to an active source of zinc; they will begin to redissolve as soon as the protective effect of zinc-rich solutions is removed.

In general, computed or experimentally determined solubilities of common secondary minerals containing the ore metals are very greatly in excess of observed concentrations of those metals in natural waters from unmineralized areas. It is possible that the identity of the most stable (least soluble) mineral of a given element in an unmineralized environment may not be known. Pyromorphite, for example, is not generally regarded as a common secondary mineral. The very low solubility of pyromorphite as compared with the more familiar oxidized lead minerals (table 5) indicates that it may be the mineral responsible for the immobilization of lead in soils and sediments. Perhaps other highly insoluble minerals, as yet unrecognized, are the hosts for traces of many other metals in soils.

Coprecipitation. — It is common to find that minerals precipitated from natural solutions will contain traces of many other elements in addition to the major components. Limonite may contain substantial amounts of arsenic, copper, and cobalt. Manganese oxides may carry barium, cobalt, and a long list of other minor elements. Barite precipitated from thermal spring water may contain significant concentrations of radium. The precipitating mineral in each case "scavenges" traces of certain elements from the solution in which it forms and incorporates them into its crystal lattice. For this to take place it is necessary that the physical properties of the scavenged ion—the ionic radius and ionic potential—lie within limits where it can readily substitute for ions of the major constituents in the lattice of the newly formed mineral. The ionic properties of radium are so nearly identical with those of barium, for example, that radium ions are quantitatively removed from solution by coprecipitation with barium sulfate, even though the concentration of radium ions is well below the limits of solubility set by the solubility product of radium sulfate.

Exotic ions may also be mechanically trapped, or occluded, within the body of the host crystal without necessarily occupying a systematic position in the crystal lattice. Simple occlusion, however, does not normally result in a quantitative removal of the foreign ions from the solution.

Adsorption. — Wherever ionic solutions are in contact with solid particles, forces of attraction are active that tend to bind the ions to the surface of the particle. The attractive force is the effect of the unsatisfied electrical charges or broken bonds on the ruptured surface of the mineral. The strength of the bond will depend on the magnitude of the surface charge and on the properties of the ion species and will be different for different ions. Also, the number of available bonds and hence the "exchange capacity," or the total number of ions that can be held by adsorption, varies with the grain size and crystal lattice of the mineral. Clay minerals and organic matter have the greatest exchange capacity, so that adsorption becomes of greatest importance in dealing with soils and fine-grained sediments that are especially rich in these materials. A measurable amount of adsorption takes place on the surfaces of all minerals, even the rock-forming silicate minerals (Sullivan, 1907). The surfaces of the root tips of plants have a particularly high exchange capacity, which assists materially in the uptake of mineral nutrients (Williams and Coleman, 1950).

Ions held by surface forces are in a state of active equilibrium with the solutions in which they are immersed. A change in the ionic content of the solutions will be reflected in a change in the ratio of adsorbed ions. In a very real sense, therefore, the adsorbed ions are still part of the aqueous system, even though they may be temporarily restricted in their movement. Adsorbed ions, by virtue of their mobility, can move through the adsorbing matrix by traveling along the surface of a particle and then jumping the narrow gap to an adjoining particle without necessarily freeing themselves of the attractive forces at the surface of the particles (Jenny and Overstreet, 1939).

The strength of the bond holding the ion to the surface of a particle is different for different ion species. The common cations have been arranged in a series of decreasing exchangeability, as follows:

$$\mathrm{Li} > \mathrm{Na} > \mathrm{K} = \mathrm{NH_4} > \mathrm{Rb} > \mathrm{Cs} > \mathrm{Mg} > \mathrm{Ca} > \mathrm{Ba} > \mathrm{H}$$

In this series, lithium has the weakest bond and hydrogen the strongest. Thus, ions to the left in the series will tend to give up their exchange positions to ions on the right. The pH of a soil is effectively a measure of the abundance of exchangeable hydrogen ions. Inasmuch as exchange reactions obey the law of mass action, increasing the concentration of an ion in the solution can effect replacement of substantial amounts of more tightly held ions. As Grim (1953, p. 144) has pointed out, there is "no single universal replaceability series. The series vary depending on the experimental conditions, on the cations involved, and on the kind of clay material."

Most field studies of adsorption and exchange capacity have been carried out by agricultural scientists, who were interested primarily in the nutrient status of soils. Ions held by adsorptive forces are as available for plant nutrition as ions in solution, and hence the exchange capacity of a soil becomes an extremely important factor in fertility. Exchange capacity is commonly expressed in terms of milliequivalents per 100 cc of oven-dry soil, and commonly ranges from 1 or less for sandy soils to 150 for some clay soils. Cation exchange capacity is generally determined by saturating the soil with ammonium or barium ions and determining the amount held at pH 7 (Grim, 1953, p. 155; Lepper, 1950, p. 41).

Absorption.—Under certain conditions, ions can enter the open lattice structure of some minerals and either occupy a void of the appropriate size or replace an ion already present. This phenomenon is observed most frequently with clay minerals of the montmorillonite group. These minerals are characterized by a relatively open lattice structure that contains passageways through which ions can enter both the spaces between the lattice layers and the layered structures themselves. The slow modification of montmorillonite to "illite" under surficial conditions is visualized as the absorption of potassium, magnesium, calcium, iron, and other cations into the relatively open spaces between the layers where they take up stable positions. In one laboratory experiment, montmorillonite and kaolinite were dried with K_2SiO_3. X-ray studies of the product showed "illite" crystal structures had been formed in the montmorillonite sample, whereas the kaolinite was unaltered (Mortland and Gieseking, 1951). Experiments in which montmorillonite is treated with aqueous zinc chloride solution show that a substantial part of the zinc ions is absorbed in a nonexchangeable form. This is interpreted as the absorption of Zn^{+2} ions into voids within the oxygen tetrahedra of the aluminosilicate lattice (Elgabaly, 1950). It is probable that many other minerals in addition to montmorillonite have the property of absorbing ions to a greater or less extent.

Absorption is most commonly shown by an increase of nonexchangeable ions in a mineral at the expense of exchangeable ions. It is, therefore, to a certain extent an empirical concept, as the content of exchangeable ions varies with the leaching reagents used in effecting their removal. Probably no clear-cut distinction is possible between absorbed and adsorbed ions, inasmuch as the exchangeability depends on the strength of the bonds that hold the ions to any given position on or within the lattice. For this reason, many workers prefer to consider the two phenomena under the general concept of "sorption."

Oxidation potential.—One of the outstanding characteristics of the environment of weathering is the abundance of free oxygen, as compared with the relative deficiency of oxygen in the environment where igneous and metamorphic rocks are formed. Many minerals that are stable under deep-seated conditions become unstable and break down under the influence of atmospheric oxygen.

The reason for the potency of oxygen to stimulate chemical reactions is its capacity to increase the positive valence state of many ions. Sulfides will tend to react with oxygen-rich waters to form sulfates, and ferrous iron will change to ferric iron. Similar reactions can take place in nature with manganese, copper, vanadium, uranium, and a host of other minor elements (Shcherbina, 1950).

The opposite of oxidation is reduction, in which the positive valence of certain component ions in the system is decreased. Reducing conditions can arise as a result of organic activity, where the oxygen has been consumed and an abundance of carbonaceous matter has accumulated. Reactions here are the reverse of those where oxidizing waters come into contact with unweathered rocks; sulfates are again reduced to sulfides, and Fe^{+3} is transformed to Fe^{+2}.

Oxidation, or the increase of positive valence of an ion, is a process of removing electrons from an ion. The oxidation of Fe^{+2} to Fe^{+3} is basically the removal of one electron from the shell of an ion, and the oxidation of S^{-2} to S^{+6} is the removal of eight electrons. Not only oxygen but any substance, such as chlorine or fluorine, that has the capacity to remove electrons from other ions is an oxidizing agent. From a consideration of the electronic nature of oxidation, it is seen that in a relatively oxidized system, the "electron escaping tendency" is greater than in a less-oxidized system. The relative freedom of the electrons can be measured by bringing a nonreactive conducting metal, such as platinum, into contact with the solution and measuring the electrical potential between the metallic electrode and a hydrogen electrode. This measurement is called Eh, and has been found to be a useful indication of the degree of oxidation of a solution (ZoBell, 1946; Castaño and Garrels, 1950; Krumbein and Garrels, 1952; Garrels, 1954).

When the Eh of an aqueous solution is raised above a certain limiting value, the water decomposes with the evolution of elemental oxygen. If it is lowered below another limiting value, a decomposition to elemental hydrogen results. These two limits restrict the range of oxidation potentials that are stable in natural aqueous solutions, and all oxidation and reductions at the earth's surface occur within this range.

The Eh at which most oxidation or reduction reactions take place varies with the pH of the solution. Except for a few reactions that are essentially independent of pH, increasing the pH of the system decreases the Eh at which the oxidation reaction can occur (Mason, 1952, p. 144). That is, making a solution more alkaline can cause the oxidation of many ions. Thus ferrous iron may be stable in relatively acid water even in the presence of abundant oxygen; if this water enters a basin where conditions are relatively alkaline, the Fe^{+2} may be oxidized to Fe^{+3} and be precipitated as ferric hydroxide. The Mn^{+2} ion is similarly stable in acid water, but with increasing pH is oxidized to Mn^{+4} which immediately hydrolyses to MnO_2, pyrolusite. In acid solutions, MnO_2 lies outside the stability limits set by the Eh of decomposition of water. Thus the presence of pyrolusite indicates that the pH of the aqueous environment in which it is formed may have been relatively alkaline.

Oxidation or reduction completely changes the species of ions involved in the reactions. In this respect, oxidation potential is different from the properties of ionic solutions already considered, where the ions retain their inherent properties throughout the various reactions and equilibria. In simple chemical reactions, the Fe^{+3} ion has no more similarity to the Fe^{+2} ion than it does to ions of magnesium or copper. Ions of each oxidation state form their characteristic dispersion patterns in the surficial environment and have their own retinue of associated elements. Under the same set of conditions, an ion of one oxidation state may be readily soluble, whereas in another oxidation state it may form extremely insoluble compounds. Oxidation or reduction, therefore, can cause almost quantitative precipitation of the reacting element. Evidence of this can be seen in the precipitation of bog manganese ores and of metallic sulfides in organic muds and shales.

An intimate association of organic activity with many oxidation and reduction reactions has been noted. Biological processes have received particular attention in considering the mode of precipitation of sedimentary iron and manganese oxides, and in the reduction of sulfates to elemental sulfur. There is no question that living processes can have a strong catalytic effect on speeding oxidation or reduction; however, they can influence only the rate of reaction. The reactions that are possible and the compounds that can be formed are restricted to those consistent with the Eh of the environment.

Inorganic complexes.—Any ion which contains several atoms, such as the sulfate ion, is a complex ion. Complex ions are more commonly thought of as combinations of simple ions, either with a neutral compound or with another ion. Examples are the formation of $Cu(NH_3)_2^+$ and $Cu(CN)_2^-$ from Cu^+. The new ionized compounds can have completely different properties than the original ions from which they were formed. The formation of inorganic complex ions, therefore, like oxidation and reduction reactions, effectively changes the species of ion and thus may modify the dispersion patterns that are formed in the surficial environment. An example of a complexing agent familiar to every mining man is cyanide, which is used to dissolve native gold from gold ore. The gold cyanide complex has chemical properties that bear no resemblance to those of the simple gold ion.

In the laboratory, extensive work has been done with the complexing effects of water, ammonia, and ions of cyanide, chloride, hydroxide, and sulfide. Very little is known, however, about the part played by complexing agents in nature, other than that they are probably extremely important factors in keeping certain elements in soluble form when by all the simple rules they should be insoluble. Some evidence for the existence of $(CuOH)^+$, $(ZnOH)^+$, and $(ZnCl)^+$ ions has been obtained in the course of studies on exchange equilibria in soils (Brown, 1950; Bower and Truog, 1940). It is probable that chloride also forms soluble complexes with copper and silver and that under some conditions sulfide forms similar soluble complexes with many metals.

Organic compounds.—Simple ions can also combine with some naturally occurring organic compounds to form so-called "metallo-organic complexes." Two principal kinds of compounds of this kind have received particular attention: the porphyrins, and soluble salts of organic acids.

Familiar examples of porphyrins in living organisms are the chlorophyll of plants with its magnesium and the hemoglobin of red-blooded animals with its iron. Porphyrin complexes with vanadium, nickel, copper, and many other metals have been identified in petroleum (Scott, Collins, and Hodgson, 1954). Similar compounds are probably present in all carbonaceous rocks containing enrichments of germanium, arsenic, vanadium, cobalt, beryllium, silver, gold, and nickel (Haberlandt, 1944). The latter writer found a gallium-porphyrin in calcite, which was proved to be spectroscopically identical with the synthetic material.

Many metals form soluble but undissociated compounds with organic acids. A common effect of the formation of organic salts, therefore, is to sequester the metallic ion so that although it remains in the solution it is not available for chemical reaction. An organic sequestering agent commonly used in the analytical laboratory is a solution containing citrate, which forms a nonionizing complex with iron under conditions where iron would ordinarily precipitate as ferric hydroxide. Organic acids have been reported as effective solvents for rock-forming minerals (Fetzer, 1946), possibly by the formation of soluble salts with the organic acid radicals. In soils, laboratory studies have shown that a great number of organic acids are capable either of "solubilizing" the otherwise insoluble mineral constituents or of preventing their precipitation from solution (Mandl, Grauer, and Neuberg, 1953). The organic acids used in this experiment are all thought to be present in natural soils.

Undoubtedly, therefore, porphyrins, salts of organic acids, and possibly other organic compounds containing metals as part of their molecular structure play a significant role in the movement of metals in the surficial environment. Some of these compounds may be soluble, and some are probably insoluble. It has been observed, for example, that organic matter is effective in decreasing the availability of zinc for plant nutrition, possibly by the formation of insoluble organic zinc compounds. The formation of metallo-organic compounds is considered responsible for the mobilization of lead in the zone of secondary enrichment in the Breckenridge district, Colorado (Lovering, 1934).

Beyond a number of empirical observations of this kind, however, the nature of the compounds actually formed under natural conditions is largely conjectural.

Colloidal solutions.—A colloidal solution, or sol, consists of a liquid medium containing dispersed solid particles larger than simple molecules, but too small to be resolved by the ordinary microscope. As so defined, the size range of colloids lies between 500mμ and 1mμ (1mμ, or 1 millimicron, is 0.000001 mm). Because of the extremely small size of colloidal particles, their movement in the liquid medium is governed more by their electrical surface charges than by gravity. As a result, suspended material of colloidal dimensions will not settle out of the liquid medium by the simple action of gravity, but will remain in suspension and move with the liquid in the same manner as true solutions.

Water is the common dispersion medium in nature. Colloidal solutions can form in the zone of weathering where material is chemically precipitated from true aqueous solutions, but for one reason or another cannot grow into large aggregates or crystals. Hydrated silica, alumina, and iron oxide precipitated during weathering may, under proper conditions, be dispersed as submicroscopic particles in a colloidal solution. Very finely divided clay minerals may also be held in colloidal suspensions. In this state, these constituents can be carried out of the system with the circulating water and do not remain behind with the other insoluble products of weathering.

Colloidal particles may be aggregated and precipitated by changing the concentration of electrolytes in the dispersion medium. This effect, however, may be offset by the presence of certain stabilizing agents, particularly organic matter, that apparently can inhibit the aggregation of colloidal particles (Moore and Maynard, 1929).

About all that is positively known of the part played by colloids in the surficial environment is that substantial quantities of colloidal material are moved in ground and surface waters, and that they are precipitated on coming into contact with the salt water of the ocean.

MICROBIOLOGICAL FACTORS AFFECTING MOBILITY

The metabolic processes of living micro-organisms have an important part to play in the dispersion of elements in the surficial environment. Micro-organisms, for purposes of this report, may be taken to include bacteria, algae, fungi, and any others of the relatively small forms of plant and animal life that inhabit soils and natural waters. Micro-organisms may modify their chemical environment either by assimilating and concentrating elements from their nutrient solutions or by catalyzing oxidation-reduction reactions.

Assimilation of elements.—Many micro-organisms have the capacity to remove large quantities of certain elements from the nutrient solution and incorporate them into their body structures.

Water organisms have perhaps the greatest effect on the mobility of elements. Riley (1939) found that a very large part of the total copper contained in the water of glacial lakes in Connecticut was tied up in the body structures of organisms in the plankton. Analysis of the fresh-water alga, *Spirogyra,* growing in mine-drainage water containing 16 ppm total heavy metals showed a concentration of 2,900 ppm zinc, 6,600 ppm lead, and 920 ppm copper in the dried algal material (Cannon, 1955). Micro-organisms have, in fact, been found to be effective agents in removing traces of radioactive contaminants from waters used to cool nuclear reactors (Ruchhoft and Setter, 1953). The enrichment of trace elements by marine organisms has long been the subject of active research and is well known (Vinogradov, 1953).

Soil micro-organisms, in addition to their effect in maintaining a physical texture that can support plant growth, can also have profound chemical effects. The most spectacular is the fixation by *Azotobacter* of atmospheric nitrogen in the form of nitrogen compounds that can be used by plants for the synthesis of proteins. The cycle of nitrogen on the earth's surface is largely due to the efforts of this micro-organism. Experiments with another species of soil bacterium, *Aspergillus niger,* show that mineral nutrients can be removed from the minerals of unweathered rocks. Bacteria grown in cultures in contact with 15 different rocks and 65 minerals extracted iron and molybendum in the largest quantities, followed in order by manganese, copper, and zinc. Igneous rocks were found to be better sources of nutrients than the metamorphic or sedimentary rocks (Swaby and Passey, 1953). Under some conditions, soil micro-organisms may immobilize the nutrient elements to such an extent that they are not available in adequate amounts for plants. An example of zinc deficiency caused in this manner is described by Hoagland, Chandler, and Stout (1937).

Oxidation-reduction reactions.—In considering the effect of micro-organisms on oxidation-reduction reactions, it should be remembered that their influence is simply catalytic, speeding the formation of products already stable at the pH and Eh of the environment in which the reaction occurs.

One important oxidation reaction is the decay of vegetable litter, whereby the mineral content originally held in the structure of the plants is released in soluble form. A tenfold increase in the copper content of stream water in the autumn has been attributed to the release of copper from rotting leaves (Riley, 1939). Variations in the potassium and nitrate content of stream waters are probably due in part to the variations in the rate of decay of dead organic matter.

The effect of bacteria in the precipitation of manganese dioxide has long been known. Mann and Quastel (1946) have found that this process takes place in two steps. First the soluble Mn^{+2} ion is oxidized to Mn^{+3}. The Mn^{+3} ion is unstable and undergoes spontaneous "dismutation" to Mn^{+2} and Mn^{+4} which immediately hydrolyzes to MnO_2. In another experiment (Thiel, 1925), manganese was precipitated by fungi from a solution of $MnSO_4$, probably as $MnCO_3$, with concomitant reduction of sulfate to sulfide.

The precipitation of iron hydroxide to form sedimentary iron formations has been attributed to bacterial oxidation of soluble Fe^{+2} to Fe^{+3} which immediately hydrolyzes and precipitates (Harder, 1919). Sulfur and zinc sulfide also can be oxidized to soluble sulfates by micro-organisms (Rudolfs and Helbronner, 1922).

Micro-organisms can also play a part in reduction reactions. Under certain conditions, bacteria can precipitate native copper (Lovering, 1927) and copper sulfide (Arkhangelski and Soloviev, 1938) from copper-bearing solutions. The reduction of sulfate to native sulfur in salt-dome cap rocks and the precipitation of pyrite in organic sediments apparently are also bacterial effects.

EMPIRICAL ESTIMATES OF MOBILITY OF ELEMENTS

In the preceding pages some of the more important factors that affect the mobility of elements in the surficial environment have been reviewed. The partition of elements between the mobile liquid phase and the relatively immobile solid phase is dependent on the interplay of these chemical and biological factors. In some environments and with some elements, the partition is largely controlled by a single one, or a simple combination, of these equilibria. In general, however, the relative mobility of an element is the resultant of such an involved combination of competing reactions that the net effect is extremely difficult to predict. It is helpful, therefore, to consider the over-all tendency of elements to move in the surface environment from a strictly empirical point of view, forgetting for the moment the physicochemical reasons for the relationships.

Mobility in normal environment.—Goldich (1938) approximated an empirical evaluation of relative mobility by comparing the composition of residual soil with that of the parent rock, the difference being the fraction of the constituents that were removed in soluble, mobile forms. He concluded that sodium and calcium are lost early in the process of weathering, whereas potassium and barium are lost later; that is, sodium and calcium are more mobile than potassium and barium.

Another approach would be to determine the amount of an element carried by rivers in soluble form as compared with the total load, including suspended and bottom sediments. Inasmuch as all the products of weathering, both soluble and insoluble, are transported in the river systems, the ratio of these quantities should give a measure of the net tendency of an element to move in soluble form. The available data on the comparative composition of the soluble and insoluble load of rivers are not adequate for such computations.

Still another method of evaluating mobility involves the ratio of the composition of the total soluble residue of river waters to that of the unweathered rocks in the drainage basin. If weathering is at equilibrium, so that all material, solid and soluble, is being removed at the same rate, this method should give the same ratios as those based only on the load of rivers. If the residual, insoluble material is accumulating in the regolith faster than it is being removed or vice versa, the ratios would be somewhat different, although the relative order of mobility should be indicated by the order of increasing ratios.

Smyth (1913) and Polynov (1937) first pointed out the significance of these ratios as a measure of the mobility of the elements in the zone of weathering. Smyth computed the relative mobility of common elements using the composition of average crustal rocks, from data presented by Clarke (1924a). Polynov has obtained similar figures for mobility by comparing figures for the average composition of igneous rocks with figures for the composition of the mineral matter dissolved in rivers whose catchment basins are mostly in areas of massive igneous rocks. Both investigators found that the common elements could be arranged in order of increasing mobility as follows: iron-aluminum, silica, potassium, magnesium, sodium, and calcium. Reiche (1950), on the basis of further computations, concluded that this order of mobility "may not hold in all situations, but if calcium, sodium, magnesium, and potassium be considered as a group, it is more mobile than silica, which in turn is more mobile than the sesquioxides Al_2O_3 and Fe_2O_3."

Theoretically, it should be possible to extend the computations of Smyth and Polynov by using the data of table 1 to derive the ratios of the minor element as well as the major-element content of river water to that in igneous rocks. Such computations do show the same general relationships that hold for the major constituents, where the elements that are commonly enriched in the soil during weathering, such as titanium, vanadium, and chromium, appear to have a lower mobility than elements like zinc and molybdenum, which are not characteristically enriched. For many of the minor elements, the reported data on the composition of fresh waters are not generally very reliable and cannot be used with confidence in computing relative mobility.

Mobility in a mineralized environment.—In geochemical prospecting, attention is focussed on the dispersion of metals from decomposing ore bodies. In the vicinity of an oxidizing sulfide deposit, the chemical reactions dominating the mobility of elements may be quite different from those characteristic of normal environments. Large quantities of both sulfate and metals go into solution in the ground water, and extreme conditions of acidity are created by the free sulfuric acid resulting from the oxidation of pyrite and marcasite. As a result, the mobility of elements in a mineralized area will be somewhat different from that in a normal, unmineralized area.

Empirical observations have been made by different workers on the mobility of the ore metals in acid mine waters rich in sulfate. Emmons (1917, p. 68-70) concluded that in the zone of secondary enrichment silver, in the absence of chloride, is more mobile than lead or gold, that copper is relatively mobile under oxidizing conditions, and that zinc is mobile in an acid environment. In his study of the Breckenridge mining district, Colorado, Lovering (1934) concluded that zinc is leached out of the surface material, whereas lead tends to be enriched, although some lead apparently moves short distances as soluble compounds formed by reaction with organic matter derived from the forest humus. In later work on the metal content of efflorescences in underground workings of the mines of the Tintic district, Utah, Lovering (1952) found that where the country rocks consist of shale and quartzite, the ore metals could be arranged in the order of increasing mobility as follows: lead, gold, copper, zinc, and silver. In fractures traversing carbonate rocks rather than shale and quartzite, silver is relatively immobile. His conclusions were based on the maximum distance from the nearest known ore that each of these metals had traveled in the solutions circulating through the capillary rock fissures. Work by the U.S. Geological Survey at the Union copper mine, Gold Hill district, North Carolina, showed that the Zn:Cu:Pb ratio of residual soil derived from the weathering of sulfide mineralization is about 10:10:30, whereas the ratio of the same elements in the unweathered ore is in the order of 10:0.6:2, with an absolute decrease in the zinc content from 4 to 0.04 percent (table 6).

From these and other data it seems safe to conclude that in acid waters rich in sulfate the order of increasing mobility of the common ore metals is lead, copper, and zinc. Lead in concentrations greater than 10 micrograms per liter is extremely unusual even in waters draining high-grade lead deposits. The relative immobility of lead in a mineralized environment may be partly the effect of the relative stability of galena as compared with other sulfides. Also, lead sulfate is much less soluble in dilute sulfate solutions than are zinc sulfate and copper sulfate. Copper is commonly an important constituent in waters draining copper deposits only where the pH is below 5.0. In normal surface waters where the pH is between 5.5 and 7.5, the content of copper is commonly below the sensitivity of the standard dithizone field method of analysis. Factors restricting the mobility of zinc do not make themselves felt until the solutions have passed well beyond the acid environment created by the oxidation of sulfides. However, as zinc-rich solutions come in contact with the fine-grained material making up soils and stream sediments, much of the zinc is apparently removed from solution by exchange reactions with particles of clay or organic matter.

Much less is known regarding the mobility of other metals derived from the oxidation of ores. The mobility of molybdenum in neutral to mildly acid solutions is probably restricted by the stability of some of the insoluble products of hydrolysis such as molybdic ochre; under alkaline conditions, molybdenum is readily soluble as the molybdate ion. The mobility of cobalt, at least in central Idaho where for some reason the insoluble erythrite is not formed, is similar to that of zinc. The mobility of arsenic is dominated by the extreme stability and insolubility of the iron arsenates that form as secondary minerals.

TABLE 6.—*Metal content of residual soils at Union copper mine, North Carolina, in parts per million*

[Chemical analyses by Laura E. Reichen, U. S. Geol. Survey, using procedure described by R. S. Holmes (1945). Auger holes were laid out in the pattern of a square, 6 feet on a side, as follows: 1 at center; 2 at northwest corner; 3 at southwest corner; 4 at southeast corner, and 5 at northeast corner]

Soil horizon[1]	Copper						Lead						Zinc					
	Auger hole number						Auger hole number						Auger hole number					
	1	2	3	4	5	Average	1	2	3	4	5	Average	1	2	3	4	5	Average
A. Residual soils over sulfide zone[2]																		
A_0	170	140	150	107	180	149	512	375	345	283	700	443	312	284	228	172	320	263
A_1	307	307	253	341	314	305	990	755	750	1,000	690	837	348	276	308	308	276	303
B_1	364	360	350	382	455	382	1,270	890	915	935	1,085	1,019	308	244	284	268	288	278
B_2	875	1,000	560	570	----	751	1,560	1,090	1,490	1,160	----	1,325	550	380	420	310	----	415
C	1,290	1,350	710	----	----	----	1,600	2,520	890	----	----	1,670	600	410	310	----	----	440
B. Residual soil over tuffaceous country rock[3]																		
A_0	17	28	17	20	18	20	104	88	104	113	80	98	148	138	124	188	212	162
A_1	21	32	21	22	24	24	183	183	198	192	182	188	140	134	140	160	150	145
B_1	34	35	32	35	34	34	225	190	305	250	200	234	156	118	150	156	136	143
B_2	43	57	78	52	55	57	265	235	910	260	190	372	146	138	210	176	144	159
C	48	72	60	73	44	59	110	155	315	245	90	183	74	94	142	144	88	108

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[1] The soil is Alamance silt loam (Allen, 1912). The horizons of the soil profile are distinguished by the following features: A_0, 0–0.5 inch humus; A_1, 0.5–2 inch gray silt loam; B_1, 2–16 inch homogeneous red to yellow silty clay; B_2, 16–29 inch mottled red to yellow silty clay; and C_1, 29–40 inch weathered rock. Samples were collected under direction of V. P. Sokoloff, U. S. Geological Survey.

[2] Sample pattern is located in undisturbed residual soil on section of U. S. Bureau of Mines diamond-drill holes 4 and 5 (Ballard and Clayton, 1948). Hole 5 intersected a zone 16 feet wide containing 0.27 percent Cu, 0.79 percent Pb, and 4.25 percent Zn, as computed from analysis of sludge samples.

[3] Sample pattern is located over tuffaceous slate about 1,300 feet north-northeast of location *A*.

SECONDARY DISPERSION

The factors that govern the partition of elements between the mobile aqueous phase and the immobile solid phase of the surface environment have been reviewed. The dispersion patterns that form as a result of this partition depend on the many different agencies that influence the patterns of movement of materials on the earth's surface.

Weathering, in the restricted sense of its definition, is only the first phase of the secondary geochemical cycle illustrated in figure 32. It is the phase dominated by the physical and chemical changes necessary to bring rocks into equilibrium with the new conditions at the surface of the earth. Movement of material in the weathering process is a minor consideration. In the later phase of the cycle, however, the physical and chemical changes that the products of weathering undergo as they are transported from their source to the site of sedimentation are influenced to a very considerable degree by the various transporting or "processing" agents. Here the patterns of flow of ice and particularly of water as it moves through soils, down drainage channels, and through the circulatory system of plants determine the dispersion patterns of the products of weathering. In presenting the principles responsible for the development of geochemical anomalies, therefore, it is more convenient to consider weathering processes first and to review the various kinds of dispersion patterns resulting from the transportation of weathering products in separate sections.

WEATHERING

Weathering has been defined by Polynov (1937, p. 12) as "the change of rocks from the massive to the clastic state." It includes the processes by which the parent rock is fragmented, and by which minerals stable in the subsurface environment are reconstituted to form new minerals that are stable in the surface environment.

The physics and chemistry of weathering have been reviewed by Reiche (1950) and for a more detailed treatment of the subject and for further bibliography the reader is referred to this excellent work.

Processes of weathering.—The dominant physical process of weathering is the disintegration of massive rocks into successively smaller fragments. Expansion of the rock due to unloading may cause cracks and joints to form. Differential expansion and contraction resulting from extremes of heat and cold at the earth's surface may also cause cracking. Expansion due to freezing of water or the crystallization of salts in cracks tends to rupture the rock further. The penetration of roots into cracks and possibly other disruptive organic activity also serve to widen the fractures already formed.

Chemical reactions resulting from contact with the abundant water, oxygen, and carbon dioxide of the surface environment are probably far more powerful in disintegrating massive rocks than the purely physical processes. Most primary minerals, being unstable in the surface environment, tend to be transformed into new minerals by hydrolysis, oxidation, and exchange reactions. In so doing, the grains expand differentially, and the rock tends to rupture along intergranular boundaries. The chemical action of micro-organisms and plant roots has a particularly destructive effect on many rock-forming minerals.

Products of weathering.—The immediate products of weathering take three forms: residual primary minerals; secondary minerals, formed at or very close to the site of weathering; and soluble material removed from the local site of weathering by circulating waters.

Residual minerals are the rock-forming minerals that are either stable in the surface environment or unstable but react so slowly that they are not appreciably broken down. The only common primary minerals that are truly stable in weathering are rock-forming clay minerals, muscovite, and probably some varieties of chlorite. Most other minerals that can withstand decomposition in the secondary cycle are inherently unstable but survive because they are chemically and physically refractory. Of these, some minerals have a greater apparent stability than others. The common minerals of igneous rocks have been arranged in the following order of increasing resistance to weathering: olivine, augite, hornblende, biotite, lime feldspar, soda feldspar, potash feldspar, and quartz (Goldich, 1938). A similar order of increasing resistance to weathering has been worked out for heavy minerals common to both igneous and metamorphic rocks, as follows: garnet, staurolite, hornblende, kyanite, monazite, sillimanite, and zircon (Dryden and Dryden, 1946). These estimates are based only on resistance to weathering and do not indicate the ability of the minerals to withstand the forces of physical abrasion in stream sediments, as will be discussed later in the section on resistant minerals in streams. Thus, although sillimanite is more resistant than garnet under purely chemical influences, it disintegrates much more rapidly than garnet when it enters the transportation phase of the secondary cycle.

Most vein-forming minerals are both unstable and extremely susceptible to decomposition in the surficial environment. Few of them survive long enough to enter the mineral assemblage of stream sediments. Outstanding exceptions are vein quartz, chert, native gold and platinum, and a few minerals of high-temperature veins, particularly cassiterite, columbite, and probably beryl. Wolframite, scheelite, and barite can withstand the chemical attack of weathering solutions relatively well, but disappear quickly during transportation of the weathering products. Sulfide minerals are particularly vulnerable to attack in the zone of weathering. The oxidation of pyrite and marcasite results in the formation of free sulfuric acid, which has the strongest corrosive effect of any naturally occurring solution. Silicates and the other sulfide minerals are attacked by the strong acid at a rate far in excess of that in a nonsulfide weathering environment. Some of the metal sulfates are readily soluble, and their removal in circulating ground water leaves voids and channels that provide further access to the system by weathering solutions. An important factor in the oxidation of sulfides is the electrochemical reaction developing in aggregates consisting of more than one electrically conducting sulfide mineral, whereby the oxidation of one mineral is favored over that of the others (Gottschalk and Buehler, 1912). Thus, in a deposit consisting of chalcopyrite and pyrite, the chalcopyrite will be oxidized preferentially with respect to the pyrite. In fact, the overall mobility of the individual metals derived from an oxidizing complex sulfide deposit is to a large extent predetermined by the relative stability of the parent sulfide minerals.

The secondary minerals formed by the weathering of primary rocks are principally the products of hydrolysis of the primary constituents. For this reason, they have been grouped together as "hydrolysates" by many workers. They include the clay minerals, a few other hydrous silicates, such as chlorite and vermiculite, and the hydrous oxides. Almost all are characterized by extreme fineness of crystal size that can usually be resolved only under the electron microscope. Clay minerals are composed, in addition to water, primarily of alumina and silica derived by the weathering of primary silicate minerals. Kaolinite is a pure hydrated aluminosilicate. Montmorillonite is an aluminosilicate in which some of aluminum in the lattice can be replaced by iron, magnesium, or zinc. "Illite" requires potassium as a necessary constituent in addition to iron and magnesium. Iron not used in the formation of clay minerals is precipitated as a hydrated oxide; manganese may also be deposited as one or more of the black hydrated oxides.

The suite of secondary minerals that forms depends to a large extent on the physicochemical characteristics of the environment. One school of soil science holds that environment—including climate, topography, and drainage conditions—is the dominant factor controlling the chemical and physical characteristics of a soil and that composition of the parent rock is of strictly secondary importance. In tropical climates an extreme manifestation of this tendency may be seen in the contrast between the weathering profile in well-drained ground where the end product of weathering is lateritic iron and aluminum oxides and that in poorly drained areas where the end product consists largely of clay minerals.

Secondary minerals formed by the weathering of ores include not only hydrous iron oxides but a host of other secondary metalliferous minerals. Unlike the clay minerals, many of these are visibly crystalline, and occur in compact aggregates that are not readily dispersed as suspensions in flowing water. Different secondary minerals are formed under different chemical environments, leading to a great diversity of mineral species. Thus, of the oxidized copper minerals, malachite will be the dominant copper-bearing product of weathering under some conditions, and chrysocolla, brochantite, cuprite, or tenorite under others. The conditions that control the stability of secondary ore minerals are principally the pH, Eh, and abundance of the reacting ions in the aqueous solutions with which they are in contact (Garrels, 1954).

The soluble products of rock weathering consist of the constituents that are released by the decomposition of primary minerals and that are not required in the formation of the new suite of stable secondary minerals. For calcareous rocks, lime and magnesia may be the principal soluble products of weathering, whereas for granites, soda and potash may be dominant.

Similarly, the soluble products of the weathering of ores consist of elements which cannot be accommodated in stable secondary minerals. Many of the secondary metalliferous minerals are stable only in the presence of solutions containing relatively high concentrations of metals. If ground-water circulation is at all active, therefore, a substantial proportion of the metals can leave the site of oxidation in soluble form. Other minerals, particularly those formed by hydrolysis under alkaline conditions, such as limonite, manganese oxides, and basic copper salts, are very sparingly soluble; where these minerals are stable, a correspondingly smaller fraction of the constituent metals will be removed in soluble form. Inasmuch as the specific reactions governing the solubility of metals near an oxidizing sulfide deposit is not generally known, it is helpful to depend on empirical observations of the mobility of metals in acid sulfate waters of the kind discussed in the section on mobility.

Relict structures and textures.—The solid products of disintegration and decomposition of rocks, before they are moved by erosive agencies, generally maintain the same internal spatial relationships as the parent material. Traces of bedding, foliation, and vein structures can commonly be followed from bedrock well up into the disintegrated residual cover. The degree to which the structures of the parent rock are preserved in the residuum depend to a large extent on the amount of compaction and slumping resulting from reduction in volume by weathering, and on the amount of distortion due to gravity movement on sloping ground.

Granite and gneiss, for example, are made up of minerals that do not change volume greatly in weathering. Thus even in areas of extremely deep tropical weathering, the primary feldspar and mafic minerals of a granitic rock may be completely altered and disintegrated without any appreciable physical movement of the constituent grains with respect to each other. The solid products of weathering retain the primary structures and textures of the unweathered parent rock, although the aggregate can be shoveled or washed as easily as an unconsolidated sand.

Calcareous rocks, however, suffer a substantial reduction in volume due to the solution and removal of the carbonate minerals. The resultant slumping causes partial or total obliteration of the original rock structures. The compaction ratio may be estimated by determining the ratio of the total volume of the original carbonate rock to the volume of the insoluble material contained in it. Where relict structures are still visible in the residuum, the compaction ratio may be approximated by observing the flattening of the dip of relict bedding or the thinning of individual beds. At the Friend's Station deposit in eastern Tennessee, a compaction ratio of 3:1 was estimated on the basis of the dip of vestigial bedding exposed along the banks of gullies (Hawkes and Lakin, 1949). In the extreme weathering of rocks made up primarily of soluble minerals, such as pure limestone and saline deposits, the negligible amount of resulting residual material commonly shows no traces of original structures.

Relict patterns of resistant minerals.—Most rocks and some ores contain primary minerals that were not completely destroyed in the course of weathering. When one or more of these minerals has a unique association with its original host, a quantitative mineralogical analysis of the residual soil may be helpful in determining the identity of the parent rock or ore. Many of the limestones of the southern Appalachians, for example, contain distinctive and readily identified types of chert. Where rock exposures are lacking, systematic examination of surficial material for fragments of characteristic chert types has been used successfully as an aid in geologic mapping. More thorough quantitative determinations of heavy minerals in soils have been found equally useful in identifying the parent rock (Marshall and Jeffries, 1945).

In prospecting, the study of heavy minerals in residual soils is probably the oldest of all methods of locating a buried lode. Gold and diamonds can be easily separated by panning, a process requiring no special training or expensive equipment. Other minerals that are more difficult to identify may call for a more technical approach. For example, the relative abundance of scheelite in residual soils can be determined by counting the fluorescent specks under ultraviolet illumination with the help of optical magnification (Sergeev, 1946b). A similar procedure has been described for prospecting deposits containing fluorescent corundum (Andreev, 1947). A systematic mineralogical analysis of residual soil for cassiterite has been used in locating bedrock deposits (Flerov, 1935, 1938).

Relict patterns of secondary minerals.—The distribution of secondary minerals in residual cover can be useful in identifying the parent rock, provided the secondary mineral can be readily identified. In many deeply weathered areas, geologists depend heavily on the color of the soil to tell them what the underlying rock is likely to be. The color of a soil is usually related to its content of limonite, a secondary mineral that may reflect the iron content of the parent rock.

Prospectors in areas of residual cover are on the alert for the tell-tale red coloration of soil, representing limonite derived from the oxidation of iron sulfides. Similarly, the conspicuous green color of secondary copper minerals is an important clue in the search for bedrock copper ore. The search for green copper in surficial material may profitably be put on a quantitative basis, as shown by C. H. White (1924) and Zenin (1935). The yellow iron arsenates, pink cobalt bloom, and many other conspicuous secondary minerals are identifying characteristics used by every seasoned prospector.

Geochemical anomalies in residual cover.—In many residual soils, the diagnostic primary and secondary minerals, if present, are too fine grained for easy identification. Chemical analysis of residual material, however, may bring out latent images inherited from the parent rock that are not obvious from casual observation.

Little use has been made of chemical analysis of soils in geologic mapping, although experimental work shows that determination of the nickel content can be helpful in identifying soils derived from serpentine (Stevens and Lakin, 1949).

In prospecting, soil analysis for traces of metals has become the most widely used and successful of the geochemical methods of mineral exploration. A great many field surveys of the metal content of residual soils over sulfide deposits have been made, and with no important exceptions the dispersion pattern of metals in the soils was found to correspond closely with the distribution of metals in the underlying rock and hence probably with that in the rock from which the soil was derived. Details of some of these surveys have been published. See items numbered 4, 5, 22, 23, 26, 27, 36, 59, 66, 85, 94, 103, 104, 108, 110, and 117 abstracted by Harbaugh (1953) and also the following: Fersman, 1939; Gilbert, 1951, 1953; Hawkes, 1954; Huff, 1952; Kennedy, 1952; Nackowski, 1952; Pierce and Dias, 1950; and Shima, 1953e, 1953f.[4]

Much of the work, however, has been sponsored by private mining companies as part of their exploration program, where commercial considerations prevent the release of information to the public.

The absolute amount of metal in the soil as compared with that in the parent rock or ore depends on the mobility of the metal, or the ease with which it is removed in solution. Thus, although an ore deposit may contain equal concentrations of lead and zinc, the derived soil may contain many times as much lead as zinc. The lead is relatively immobile and is retained, whereas the zinc tends to be leached out. In general, it is found that

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[4] See also footnote 1 on p. 234.

lead, tin, arsenic and antimony are immobile and are held in the residual soil; zinc and cobalt tend to be impoverished; copper, tungsten, and molybdenum appear to be intermediate.

Although the major part of the mobile metals dissolved from the weathering products of a vein is entirely removed, a significant part may be transported in solution only for short distances and then reprecipitated locally. The effect is a lateral and downhill spreading of the dispersion pattern outward from the bedrock source. Zinc anomalies hundreds of feet wide have been observed in residual soil associated with veins measuring only tens of feet in width. The lead anomalies over the same veins were not only much narrower but corresponded much more closely with the location of the vein. Over such a vein, samples spaced at 100- or 200-foot intervals would have been adequate for locating the zinc anomaly, whereas a 50-foot spacing would have been necessary for the lead anomaly. It has been the writer's experience, therefore, that where complex ores containing two or more metals are sought, greatest economy is achieved when reconnaissance geochemical soil surveying is based on the more mobile metal and detailed work is based on the less mobile one.

The homogeneity of a metal pattern in residual soils is apparently also related to mobility. The characteristically homogeneous patterns formed by mobile metals such as zinc indicate that original local and erratic variations in the distribution in soils of the mobile metals tend to be smoothed by solution in rich spots and local redeposition in lean spots. With immobile metals, solution is inhibited and the original spottiness of distribution is preserved. Thus Tikhomirov and Miller (1946) report that the molybdenum pattern over the Kounrad molybdenite deposit is less erratic than the tin patterns commonly found over cassiterite veins. The relative homogeneity of a geochemical anomaly is an important consideration in determining the most efficient spacing of samples in practical survey work. An anomaly defined by a mobile metal with its more homogeneous pattern can be located and mapped with fewer samples than an anomaly defined by an immobile metal.

Geochemical anomalies in residual cover may be distorted by downslope movement of the soil. The result is an asymmetrical curve in which the metal content falls off less rapidly on the downhill side than in the uphill side, as illustrated in the diagrams presented by Huff (1952). Asymmetry of this kind can also be caused by the action of metal-rich solutions depositing metal in the soil on the downslope side, although the net effect is the same whatever the cause. In extreme cases of asymmetry owing to downslope movement, geochemical anomalies may be detected by sampling along the foot of a slope, hundreds of feet below the outcrop of the vein. Riddell (1954) describes reconnaissance exploration work in an area of high relief by systematic sampling of soils barely above the modern stream terraces.

Patterns in residual soil may also be distorted by compaction slumping. At the Friend's Station deposit in eastern Tennessee, an average of 50 feet of residual clay overlies a gently dipping limestone sequence. The clay overburden was estimated to represent the weathering product of three times its volume of parent rock. The resulting flattening of the dip of the gently dipping ore caused the geochemical soil anomaly to come to the surface several hundred feet on the footwall side of the suboutcrop of the ore (Hawkes and Lakin, 1949).

Gossans.—A gossan is the mass of residual limonitic material that remains behind after removal of the soluble products of weathering of a sulfide-bearing deposit. Being residual, gossans can be traced downward through successively less weathered zones into the unweathered primary sulfide minerals. Historically, gossans have been one of the best guides to the prospector in areas of residual cover and deep weathering.

At the surface, blocks of gossan material may be dislodged from the main mass and scattered over the immediate vicinity by frost action, slumping, and slope creep. If the fragments are sufficiently durable, they may on occasion be transported for substantial distances by glaciation or stream action. Studies of the dispersion pattern of limonitic fragments, particularly in alluvial material, have led many prospectors to the parent gossan mass and the hidden sulfide deposit beneath.

The necessary prerequisite for the formation of a gossan, in addition to deep weathering and an oxidizing environment, is the presence in the bedrock of iron as sulfide or carbonate to provide the raw material for the formation of limonite. The common gossan-making minerals are pyrite, marcasite, pyrrhotite, copper-iron sulfides, arsenopyrite, siderite, and ankerite. In general, the more iron is present in the primary ore, the more pronounced will be the gossan. The occurrence of economically valuable metals in the ore is only indirectly related to gossan formation, in that ore minerals are commonly associated with the gossan-making iron sulfides and carbonates. Thus not all gossans indicate base-metal sulfides, and many base-metal sulfide deposits do not weather to form gossans.

The mineralogy of gossans is limited to species that are stable in contact with acid sulfate solutions. The dominant minerals are limonite, quartz, and secondary silica. The overwhelming abundance of limonite is responsible for the conspicuous red-brown to black color of gossans, a feature difficult to overlook even in a casual reconnaissance of an arid terrane. Depending on the parent material and the maturity of the gossan, barite, gypsum, jarosite, secondary metalliferous minerals, and clay minerals resulting from the breakdown of the country rock may also be present. Secondary green copper minerals in a gossan may be a useful indication of the presence of copper in the primary ore.

The structure and texture of gossans, to a greater or less extent, reflect the original characteristics of the parent material. The primary ore minerals in the course of weathering may form minute, tabular veinlets of silica or limonite along crystal directions. These systems of veinlets may remain behind after the original mineral has been completely destroyed, leaving a boxwork pattern that is characteristic of the primary mineral. Distinctive boxworks indicative of most of the common sulfide minerals have been identified and described by Blanchard and Boswell (McKinstry, 1948, pp. 268-276), and have been used widely in appraising leached outcrops in terms of the commercial grade of the primary sulfide deposit.

The chemical composition of gossans has received far less attention than their mineralogy and texture. What little evidence has been reported to date, however, points to the conclusion that the content of traces of the ore metals in the limonite of gossans can be used to indicate the relative abundance of those metals in the primary deposit. In the Nyeba district of Nigeria, samples of limonite from a gossan over a deposit known to contain lead and zinc, contained on the order of 4,000 ppm lead and 500 ppm zinc. Similar samples from an undeveloped prospect where a geochemical soil survey showed the presence of zinc but no lead contained on the order of 50 ppm lead and 8,000 ppm zinc (Hawkes, 1954).

GLACIATION

The grand scale of movement of the continental ice sheet is attested by the identification of glacially transported erratics that have been dropped hundreds of miles from their source. Fragments of native copper derived from the Keweenaw

Peninsula of northern Michigan have been found as far south as southern Illinois, and a boulder of a distinctive norite gneiss from near the city of Quebec has been picked up in southern Ohio some 700 miles away (Flint, 1947, p. 118). The bulk of the material in glacial tills, however, is of relatively local origin. Chamberlin (1883) estimated that 90 percent of the material in the moraines of southern Wisconsin traveled less than 1 mile, and studies of the glacial boulders in northern New Brunswick show that the most abundant rock type is a fairly reliable indication of the lithology of the bedrock directly beneath. Thus, although a few glacial erratics have traveled a very great distance from the source, the overwhelming majority of pebbles and boulders contained in glacial till are of local origin. It is possible that the bulk of the rock load of the continental ice mass was contained in a lower layer that moved relatively little and was overridden by a layer of cleaner ice carrying relatively few boulders but for far greater distances.

The direction of movement of continental ice during a single glacial epoch is generally outward from a central area in the heart of the ice mass. At any one locality, however, the direction may fluctuate somewhat around a mean value, with the result that glacial erratics are commonly distributed in the form of a fan spreading from the source in the direction of ice movement, rather than as a linear pattern. The prerequisite for the formation of a simple fan-shaped pattern of glacial dispersion is the existence of a relatively small area of outcrop of a unique, mechanically resistant, and readily identified rock type. In New England alone, well-defined glacial fans have been mapped in association with nine ocurrences of distinctive rock types (Flint, 1947, p. 120). In Scandinavia, similar studies of glacial dispersion of rock fragments consistently reveal the same characteristic fan-shaped pattern (Lundqvist, 1935; Högbom, 1931).

Following the principle that the source of glacially transported boulders of an unusual rock type should be at the apex of a fan-shaped distribution pattern of similar boulders, prospectors in glaciated countries, especially in Scandinavia, have systematized the search for glacial ore boulders as an aid in exploration. A substantial number of important discoveries resulting partly or entirely from the use of this technique have been reported from Scandinavia (Grip, 1953; Högbom, 1931; Ödman, 1947; Sauramo, 1924). In North America, the discovery of the Steeprock Lake iron deposit in western Ontario started with the observation of glacial erratics of iron ore south of the point where the bedrock ore was later found (Bartley, 1940).

If glacial movement can form a fan-shaped pattern of ore boulders, it is reasonable to expect that the chemically determined metal content of the fine-grained fraction of the till will show a similar pattern. Presumably, the sand and silt-sized fraction of till is derived in large part from the preglacial regolith which may contain gossan and other metal-rich preglacial dispersion patterns related to the ore. A variable amount of finely pulverized primary ore may also find its way into the fine-grained fraction of the till. This possibility is still largely in the realm of speculation, as glacially transported metals in the fine-grained fraction of tills have been identified in only a few areas. In the vicinity of the sulfide deposits of the Bathurst district of New Brunswick, the patterns, in addition to the strong homogeneous anomalies closely related to the ore, consist of extremely erratic, local areas of high metal content scattered in a crude fan-shaped arrangement lying to the east of the source. From this it may be assumed that the direction of ice movement was from west to east, although corroborative evidence is difficult to find. Between the local anomalies which are perhaps 50 feet across on the average, the metal content of the till is not appreciably above background level. Test pitting at one local geochemical anomaly in New Brunswick uncovered till containing a few cobbles and pebbles of massive pyrite, barite, and high-grade galena ore, together with the usual assortment of locally derived unmineralized rocks. In the Røros mining district of Norway, Vogt and Bergh (1946, 1948a, 1948b) have described a somewhat similar distribution pattern of copper, zinc, lead, iron, and manganese on the down-glacier side of a known sulfide occurrence.

The source areas of alpine glaciers, in contrast to continental ice masses, are limited to the drainage basins within which they lie. For this reason, studies of terminal valley moraines might be a simple and rapid method of determining what kinds of rocks and ores occur within a well-defined area of considerable extent. Kreiter (1940, p. 170) mentions the occurrence of boulders of vein quartz in the moraine of a valley glacier at Iak-su in Russia. So far as the writer is aware, however, no use has been made of the distribution of chemically determined metals in valley morainal material as a method of prospecting.

FROST ACTION

The action of frost in moving and sorting surficial material involves a combination of movement by growing ice crystals and by the water that forms the ice and is released when the ice melts. Experiments have shown that a growing frost crystal is fed by soil moisture moving upward from below, where temperatures are not sufficiently low to freeze the films of water on the surface of the clay minerals. The growing crystals thus act as collectors and concentrators of moisture gathered from a considerable volume of material. Any salts dissolved in the soil moisture are enriched in the aqueous phase as the water is removed to feed the frost crystals. As the crystals grow they exert pressure on the surrounding solid fragments, causing minor readjustments in the relative position of the fragments and keeping them in open packing. When the ice melts, the pressure is released and the water concentrated by the frost-forming process forms a mobile slurry with the silt and clay from the surrounding material. The total effect of this process repeated over a period of many years is a turbulent mixing of the surficial material to the maximum depth of the frost action. If the angle of slope is sufficient, a downslope movement is combined with the turbulent mixing, and the finer grained materials may be removed completely in the muddy water that drains out after the melting of the frost each spring. Under proper conditions the meltwater from the frost may mobilize a large mass of unconsolidated material, which then can move down the slope as a mudflow or landslide.

In geochemical prospecting, the turbulent mixing and downslope creep of surficial material owing to frost action is a factor deserving special consideration, at least in some areas. The Blackbird cobalt district of Idaho, where extensive experiments in geochemical prospecting methods were conducted by the Geological Survey, is in an unglaciated area of deep weathering where the zone of frost mixing extends commonly to a depth of about 4 feet.[5] The maximum intensity of frost activity probably coincided in time with periods of active glaciation elsewhere. Mineral exploration by conventional methods in this area was hampered by the scarcity of outcrops and especially by the virtual absence of fragments of oxidized ore or gossan in the surficial material overlying the cobalt deposits. Well-developed gossan, however, could be observed in the undisturbed weathered rock immediately below the zone of frost action. Very probably one of the effects of frost action was to disintegrate the soft limonitic fragments derived from the weathered rock into fragments too fine grained to be identified in the zone of frost mixing. Soil analysis for copper and

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[5] See footnote 1 on p. 234.

cobalt showed strongly developed and homogeneous dispersion patterns. Undoubtedly, the homogeneity of the patterns was at least in part the effect of the mixing action of the frost. On some of the steeper slopes, however, the patterns were difficult to interpret in terms of what was known about the distribution of bedrock ore. These were places where the topography indicated landslide activity, possibly resulting indirectly from frost action.

ANIMAL ACTIVITY

Although man, of all the animals, has assumed the most spectacular role in the transportation of surficial deposits, many other species have played an equally important part as far as the total effect is concerned. In many climates earthworms are continually churning the soil near the surface. Burrowing animals, such as foxes and woodchucks, bring material to the surface from deeper parts of the weathering profile. Ants and termites, especially in tropical countries, excavate huge labyrinths often extending to great depths, from which they carry the material to the surface. Although the transporting effect of any one individual or colony may be trivial, the effect of such activity over thousands of years may be a very substantial factor in the mixing of the components of the weathering profile.

In many areas of deep weathering, prospectors have profitably searched through the material brought to the surface by burrowing animals and insects for fragments of gossan or oxidized ore minerals. Analysis of ant heaps for traces of ore metals as a method of prospecting has been attempted in Africa and Australia, but no report has yet been published on its success.

SOIL FORMATION

The upper few feet of the earth's surface comes under the influence of a complex series of reactions that transform the raw fragmental material resulting from rock weathering into a medium that can support plant growth. The process, known as soil formation, is thought to be primarily the work of bacteria and fungi that derive their vital energy from the oxidation of dead plant remains. The result of the soil-forming process is the differentiation of the surficial material into distinctive layers or soil "horizons." The vertical section through the sequence of soil horizons is commonly known as the soil "profile."

The principal horizons of the soil profile are the uppermost "*A*" horizon, or topsoil; the "*B*" horizon, or subsoil; and the "*C*" horizon, or parent material that has not been affected by soil-forming processes. In detailed descriptions of soil profiles each of these horizons may be divided into smaller units on the basis of local minor variations in color, texture, or composition. These subdivisions are commonly designated by subscripts; B_1 and B_2 are thus subdivisions of the *B* horizon. The humus layer, which constitutes the topmost member of the *A* horizon, is commonly designated as the A_0 horizon. The *A* horizon is characterized by a leaching of certain elements which move downward to be precipitated in the *B* horizon. The *C* horizon, or parent material, is usually weathered rock or residuum; the depth to the *C* horizon has no direct relation to the depth to the unweathered bedrock.

Different elements take part in this process in different climates. In moist temperate climates, iron and aluminum oxides tend to be leached from the *A* horizon and reprecipitated in the *B*, a process known as podzolization. In moist tropical climates, silica as well as iron and alumina take part in the formation of the so-called lateritic soils. In arid climates, the leaching and reprecipitation of calcium within the soil profile is an important factor.

The importance of soil-forming processes in geochemical prospecting is that they may modify anomalies that have formed in either residual or transported cover. This effect is particularly apparent in temperate forest soils, where the topsoil or *A* horizon may be so leached that samples of this material cannot be effectively used for geochemical mapping. A zinc anomaly in residual soil over the Friend's Station deposit in Tennessee was clearly defined by samples taken from the *B* horizon at a depth of 4 feet; the same area sampled from the *A* horizon at a depth of 2 feet showed a very inhomogeneous and erratic pattern of zinc distribution. The difference was thought to be entirely the effect of leaching of the zinc from the upper topsoil horizon (Hawkes and Lakin, 1949). The copper, lead, and zinc contents of soil profile over ore and over barren ground at the Union copper mine, North Carolina, are given in table 6. The data for normal soil show leaching of copper and lead in the *A* horizons, an enrichment of lead in the *B* horizons, and an enrichment of zinc in both the *A* and *B* horizons as compared with the parent material. The almost consistent increase of all metals with depth in the anomalous profiles is noteworthy. These data confirm the general experience that the *B* horizon of forest soils is somewhat more reliable for geochemical sampling than the *A* horizon. Work in other types of soils, however, has not indicated any variations in the distribution of metals in the soil profile that need to be taken into account in geochemical survey practice, so that samples taken from any part of the soil profile can be used equally well in geochemical soil surveys. For example, Huff

(1952), in working with immature Rocky Mountain soils, found that samples of surface soil were just as satisfactory as deeper samples and were much easier to collect.

The data of table 6 also show the lateral variation of metal content within the same soil horizon. The distribution of metals in the *A* and *B* horizons is considerably more homogeneous than in the *C* horizon, indicating that the near-surface horizons are more suitable for geochemical surveying than the deeper material. The lateral variations within short distances are far greater than the variations of replicate determinations by the analytical methods used in this experiment but are roughly equivalent to the variations of replicate determination by the less precise rapid methods in general use in geochemical prospecting.

UNDERGROUND WATER MOVEMENT

The movement of water under the influence of gravity or of a hydrostatic head is a fairly simple matter of flow from a higher to a lower level, or from an area of higher to an area of lower pressure. Rainwater soaks into the soil and replaces the air in the pore spaces of the surficial material or rock; in the upper unsaturated section of the mantle it is known as vadose water. If the pore spaces extend to sufficient depth, the rainwater eventually reaches the water table, which is defined as the surface below which the air in the pore spaces has been completely replaced by water. The ground water, or water below the water table, then tends to move laterally in the direction of the easiest means of escape. It may emerge at the surface as springs and as seepages along the banks or in the beds of streams. Under ordinary circumstances, a swamp, spring, or stream is in effect an "outcrop" of the water table. In climates with sufficient rainfall, the water table slopes in essentially the same direction as the surface of the ground, and its contours are about parallel with topographic contours. In some areas of deficient rainfall, however, the river water may actually flow back into the ground, with the effect that the water table slopes away from the riverbed rather than toward it.

The gravity movement of ground water is impeded by the material through which it flows. Fresh rainwater entering the underground reservoir of the ground-water system cannot escape as fast as it is added and tends to pile up. The effect of this piling up is to raise the water table so that higher escape channels are available, and new springs and seepages become active. Conversely, during a period of light rainfall, the water table will be lowered and springs will progressively dry up.

In areas of crystalline or metamorphic rocks which have negligible pore space, a true water table may not exist unless the cover of surficial material is deep enough. Here, rainwater that has soaked into the soil tends to flow along channels on the surface of bedrock. When a channel of this kind crosses a permeable zone of fracturing or shearing, the water may enter the fractures to emerge again at the surface of bedrock at a lower elevation.

Water and the salts dissolved in it can move against the force of gravity by capillary rise, by diffusion, and by migration of ions on the surface of minerals, as discussed in an earlier section. These effects are most pronounced in the unsaturated fringe zone of vadose water between the water table and the land surface. The net result of movement against the force of gravity is commonly a dispersion of the dissolved constituents both upward and laterally in the direction of decreasing concentration.

Upward dispersion of this kind may be accelerated by the pumping action of a periodically rising and falling water table. Water in the fringe zone moves downward as rainwater soaks in from above; in dry periods, the direction of movement is reversed in order to replenish the moisture removed nearer the surface by evaporation and transpiration. Thus the movement of moisture in the fringe zone pulsates with the weather, moving downward during rainy weather and upward during dry weather. At any given time, the direction of movement of this pulsation is thus the opposite of the movement of the water-table surface, which rises in rainy weather and falls in dry periods. The over-all effect of this pumping action is a spreading of dispersion patterns upward from the source in the bedrock.

The elements that can move readily in ground water and soil moisture are in general the elements of high mobility, such as zinc and cobalt. The dispersion patterns formed by them can, of course, be mapped directly by sampling and analysis of the water itself. They can also be mapped by measuring the exchangeable cations in the material through which the solutions percolate. Solutions containing metals derived from the weathering of a sulfide deposit, as they come in contact with permeable, unconsolidated sediments or residual soils, set up exchange reactions whereby the metal content of the matrix is increased at the expense of the metal content of the solutions. In the course of time, an equilibrium between the adsorbed ions in the matrix and the dissolved ions in the solutions will be reached. As this equilibrium is approached, the pattern of dissolved ions spreads farther from the source into fresh material, until that again is saturated with exchangeable metallic ions. In this way, a pattern of dispersion grows in the matrix that is an exact replica of the pattern in the water. Because patterns of this kind are superimposed upon whatever dispersion patterns were originally present in the matrix, they have been termed "superimposed" halos by Russian workers (Sergeev, 1941, p. 38 of translation).

In geochemical survey work, it is rarely practicable to collect soil moisture for analysis. Superimposed halos can be readily mapped by simple chemical analysis of the matrix, however. Inasmuch as the superimposed halos are fossilized replicas of the water pattern, they are extremely useful in tracing the channels followed by the soluble products of decomposition of ore bodies.

Geochemical anomalies developed by movement in underground water have somewhat different characteristics depending on whether they occur in descending or laterally moving ground water, spring water and seepages, or vadose water.

Descending ground water.—Descending ground water can be sampled conveniently only in the underground workings of mines. The composition of aerated water descending through cracks and fracture zones in the rock will in general reflect the chemical character of the rock or ore through which it has passed. Lovering (1952) has shown that the metal content of descending water in the relatively dry mines of the Tintic district, Utah, reflects the presence or absence of ore in the channels through which the water has passed. He found that the composition is modified by the chemical character of the rocks adjoining the channels and by the distance traveled by the solutions. Japanese workers found a correlation between the content of iron, zinc, and sulfate in fracture-zone waters, and the occurrence of known ore above the underground workings in which the samples were collected (Kimura, Fujiwara, and Morinaga, 1951). On the basis of data of this kind, at least one body of ore has been discovered (T. Watanabe, oral communication, 1953).

A commonly observed pattern formed by descending ground water is the zone of secondary enrichment in large sulfide deposits. Downward-moving water above the water table leaches copper from secondary copper minerals. As these copper-rich solutions pass downward into the zone of primary sulfide minerals, the copper in the solution reacts with the primary chalcopyrite to form secondary copper sulfides, such as bornite or chalcocite. Zones of secondary enrichment make up the best grade of ore in many of the western porphyry copper deposits (Emmons, 1933).

Laterally moving ground water.—Many workers have made systematic studies of the metal content of well water, and some of them have reported positive correlation with known ore. Rarely, however, has it been possible to forecast the occurrence of an unknown body of sulfide ore from well-water data. Part of the difficulty is perhaps the almost universal presence of artificial contamination of the well water by copper and zinc from pumping equipment and other plumbing in contact with the water. Such contamination causes large erratic variations of no significance that mask the minor variations in metal content due to increments from decomposing sulfide minerals. Another reason for failure in some areas is that the water has been sampled below the zone of oxidation where the metal from primary sulfide is not actively going into solution. Kennedy (1956) collected water from churn drill holes in and near an undeveloped zinc deposit in southwestern Wisconsin and found that the zinc content was hardly above the background; the ore body there, however, is well below the lowest level of the water table. In other areas, the pH of the ground water may account for the failure of metal to appear in well water. Lovering, Huff, and Almond (1950) report that the copper content of water from exploration holes cutting copper ore at the San Manuel deposit, Arizona, was below the limit of detection. The pH of the water averaged 9.0, well above the pH of hydrolysis of copper in dilute solutions (table 4). Although the results of experimental well-water sampling have to date been uniformly discouraging, this approach perhaps should not be completely abandoned until more investigations have been made with proper respect for the necessary precautions.

Superimposed halos in the rocks or surficial material through which the ground water has passed have been observed in many areas. At the Ray Copper deposit in Arizona, Clarke (1935) described copper in the form of tenorite in the postore Whitetail conglomerate. The distribution pattern there indicates that the tenorite was deposited from copper-rich ground water derived from the oxidation of the main ore body. The maximum copper content of this secondary deposit is about 5 percent, or more than twice that of the better-grade ore in the mine.

Sampling alluvial cover over a lead-zinc vein in the Abakaliki district of Nigeria (Hawkes, 1954) showed a well-defined zone of lead- and zinc-rich material immediately above the surface of bedrock leading away from the suboutcrop of the ore in the direction of the drainage channel; on the other side of the sub-outcrop, away from the drainage channel, this pattern was lacking. Presumably the movement of ground water here was controlled largely by the bedrock surface, as the underlying shale was unweathered and relatively impermeable to percolating solutions.

Spring water and seepages.—Analysis of water from cold springs and seepages has been considerably more successful than well-water studies in indicating unknown deposits of ore. The danger of artificial contamination of spring water is very slight, except for springs in limestone country where the spring is effectively the point of emergence of an underground stream. Also the water from springs is drawn from near the water-table surface, where oxidation and solution of primary sulfide minerals is most active, rather than from some unknown depth below the water table as is the case with well water. Many springs discharging metal-rich water have been correlated with known sulfide deposits within the source area. Other metalliferous spring waters occur in mineralized districts where the occurrence of sulfide ores is highly probable. In a few such areas, later exploration above the spring has uncovered sulfide occurrences. At least in noncalcareous terrain, no example of a metal-rich cold spring water has been reported where the absence of sulfide minerals in the bedrock has been definitely proved.

Superimposed patterns are commonly developed in the soil and muck around metal-rich springs or seepages where metal has been adsorbed in the solid material through which the solutions have percolated. Inasmuch as the pattern of exchangeable metal will be retained even when the seepage is inactive, soil analysis is a relatively dependable method of determining the relative metal content of the solutions that have been in contact with it.

Seepages commonly occur on the edges of modern alluvial flats, where ground water containing the soluble products of weathering discharges into the surface drainage. Seepage areas also may occur scattered on the hill slopes above the drainage channels where they may be identified either by the nature of the soil or by characteristic types of vegetation. Trace-metal analysis of soil and muck around ground-water seepages may indicate whether the water has passed through an area containing actively oxidizing surfaces. Geochemical anomalies of this kind would, of course, indicate a source in a direction up the slope of the water table from the seepage rather than directly underneath.

Examples of what are probably superimposed seepage patterns have been reported by Bischoff (1954) in his work on geochemical soil sampling over base-metal deposits in eastern Canada. He found that the geochemical anomalies in samples of near-surface glacial material were commonly displaced as much as several hundred feet downslope from the suboutcrop of the sulfide vein. Presumably these anomalies represent the points of emergence of ground water that had been enriched in metal by passing through the oxidizing deposit.

Below the Chicago-Brown Bear ore zone at the Blackbird cobalt district of central Idaho surficial rubble has been cemented by limonite rich in copper and arsenic. The cementing material was most probably derived by precipitation from metal-rich ground waters that had filtered through the pyritic copper-cobalt mineralized area. Very possibly many limonitic breccias generally included with gossans are in reality precipitated from ground waters.

Organic soils provide a particularly favorable host for superimposed halos. Under certain conditions the decay of dead vegetable remains is inhibited for one reason or another, and a considerable thickness of organic matter may accumulate. In northern climates, this process leads to the formation of peat deposits and muck bogs. Probably by a combination of adsorption and the formation of stable insoluble organic complexes, many elements are precipitated in the presence of organic matter. Any metallic ions that enter such an environment in ground or surface waters tend to be immobilized and strongly concentrated in the organic matrix.

At the Manning muck bog near Albion in western New York, Cannon (1955) describes a distribution of zinc along the edge of the bog and around springs that discharge through the central parts of the bog. The zinc is apparently precipitated from zinc-rich ground water at the point where it first comes in contact with the organic environment. The ultimate source of the zinc is the Lockport dolomite, which is locally enriched in sphalerite. Several million pounds of zinc have been precipitated in an area of less than 1 square mile. The average dry weight zinc content of the muck in this area is 0.5 percent, and maximum zinc contents of more than 10 percent have been reported.

Salmi (1950), in determining the metal content of peat from 49 bogs, in Finland and Norway, found that the metal content of bogs in mineralized areas was significantly higher than in barren areas. He concludes that 0.1 percent copper and 0.6 percent zinc in peat ash indicate rock mineralized respectively with copper and zinc, and that 0.03 to 0.1 percent nickel could be regarded as an indication of nickel-bearing ore. The background copper, zinc, and nickel content of peat is, respectively, 0.03, <0.03, and 0.01 percent.

Vadose water.—The processes already described whereby dissolved salts move upward against the force of gravity can result in a pattern of dispersed metal in the surficial material directly over the source in the bedrock. Although ionic diffusion is probably only one of the mechanisms responsible for upward movement, it is convenient to refer to the resulting dispersion patterns as "diffusion patterns."

Diffusion patterns are best developed in a matrix containing a substantial proportion of clay-sized particles. The fine-grained matrix has both a higher retentivity for water and a higher exchange capacity, so that the dispersion patterns can be readily fixed as superimposed halos. Fine-grained alluvial and glacial deposits are relatively good hosts, whereas sand and loess are poor hosts. Diffusion halos undoubtedly form also in residual soils but are masked by the inherited patterns of residual metals.

In the Austinville zinc district of Virginia, Fulton (1950) reports a distribution of zinc in Tertiary river sediments that closely reflects the zinc content of the underlying mineralized bedrock. Patterns of this kind were lacking in the most recent river sediments, where presumably the shortness of time had not permitted the maturing of the diffusion pattern.

A well-defined example of a diffusion pattern was mapped in detail in the Abakaliki lead-zinc district, Nigeria, where relatively unweathered bedrock was overlain unconformably by a 6-foot deposit of alluvial silt (Hawkes, 1954). Sampling on a vertical section through the silt as exposed in an exploration trench showed an easily contoured distribution of zinc, falling off uniformly with distance from the underlying source from a maximum of several thousand parts per million directly over the ore to several hundred at the surface. Historical evidence indicates that the silt in which this pattern was formed was deposited about 400 years ago, so that an estimate of the time required for the evolution of a diffusion pattern can be made.

Somewhat similar patterns, although not as clearly developed, have been found in the course of experimental work in glaciated terrane in the United States and Canada. White and Allen (1954) report copper in glacial till over what is probably a leakage halo in the rocks overlying the Deadwood Camp deposit in British Columbia. Some of the anomalies in glacial till over mineralized zones illustrated by Bischoff (1954) may be, at least in part, diffusion halos. Some of the best examples of diffusion halos in deep glacial cover have been found in the course of commercial exploration work, the results of which are not available.

Work by Kennedy (1956) in the driftless area of southwestern Wisconsin has failed to find any evidence for superimposed halos in the loess cover. A zone of mechanically mixed loess and residuum occurs commonly at the base of the loess blanket, where any anomalies present in the residuum are dispersed into the mixed zone. This, however, has been interpreted as a simple mechanical mixture of metal-rich residuum and barren loess, and not as the effect of migrating ions or solutions.

VEGETATION

The principles underlying chemical or botanical studies of vegetation as a method of locating buried ore deposits are basically simple. The root systems of trees can be portrayed as powerful sampling mechanisms, bringing representative solutions up from a large volume of ground below the surface. Then, as the water is removed by evaporation, the mineral content of these solutions is left behind and concentrated in the leaves.

In detail, however, the circulatory system of terrestrial plants is by no means simple. A vast and complex set of equilibrium relationships is active from the time the nutritive solution comes within the influence of the root tip until the water is discharged into the atmosphere. Whether or not a metal-rich nutrient solution will be reflected by an easily measured variation in the composition of the plant, or by a diagnostic variation in plant morphology or ecology, depends on the balance of these many relationships.

In reviewing the factors causing plant anomalies, it is pertinent to consider (1) the availability of elements in the soil, (2) the factors governing the movement of solutions into plants, (3) the movement of and nutritive effect of mineral matter within plants, that is, plant nutrition, and (4) the chemical and biological effects of this process that can be used as guides to the prospector. As a result of recent research, much of it aided by radiotracer techniques, the physics and chemistry of some of these reactions are beginning to be understood (Truog, 1951).

Availability of elements in soil.—Agricultural scientists refer to "available" nutrients, which consist of ions either dissolved in the soil moisture or adsorbed on the clay minerals of the soil. These nutrients constitute the mineral content of the soil that is immediately available for uptake by the plant. They make up only a small proportion of the total mass of the soil, the remainder of which consists of ions tightly bonded within the lattice structures of the stable soil minerals.

Availability of an element to plants is measured either by determining the amount of the element that can be removed from a soil by leaching with chemical reagents, or by growing a plant in the soil and determining the amount of the element taken up by the plant.

Availability is a concept closely related to mobility in the surface environment. It can be regarded as the mobility with respect to plant activity. The ratio of the availability to the total content of an element in the soil is a function principally of the soil pH, oxidation potential, exchange capacity, and presence of complexing agents. Artificial modification of one or more of these factors can under many conditions change the nutritive value of a soil. For example, the available molybdenum can be increased by adding lime and thus increasing the pH to a point where the molybdenum already present becomes soluble (Evans and others, 1951). The addition of lime has also been recommended as a cure for soils poisoned by an excess of available zinc, because of the lessened solubility of zinc at a high pH. Adding animal fertilizer to a soil in one experiment was also found to reduce the availability of zinc, probably by the formation of stable organic zinc complexes. The effect of complexing agents is illustrated by the use of synthetic metallo-organic complexes (specifically, the metal salts of ethylenediamine tetraacetic acid) as an artificial source of minor-element nutrients; added to a soil, these complexes are just reactive enough to provide the plant with an adequate source of the element but not so unstable that the element is largely leached out with the first rain, as would happen if it were present as soluble salts.

Movement of soil solutions into plants.—According to currently held concepts, the surface of the root tip of a plant and the immediately surrounding solutions are characterized by a high concentration of hydrogen ions. This effect is so local that it is not apparent from a measurement of the pH of the soil as a whole. The cause of the enrichment of hydrogen ions is probably the hydrolysis of CO_2, which escapes through the roots in substantial quantities (Burd, 1947). The effect of the H^+ abundance is to set up active cation-exchange reactions between the clay minerals of the soil and the surface of the roots, which have been shown to have a high exchange capacity (Williams and Coleman, 1950). On the surface of clay minerals, hydrogen ions exchange for metal ions which then move through the soil to the roots, probably by a combination of diffusion, surface migration, and contact exchange (Jenny and Overstreet, 1939). When the metal ions reach the outer surface of the root tip, they exchange for hydrogen ions, which are then released to repeat the process.

Empirical observations have shown that the local but extremely corrosive environment near the root tips of plants can extract mineral matter well in excess of what is present in readily exchangeable form. Even primary minerals such as feldspar can be broken down and their component cations made available to the plant (Keller and Frederickson, 1952). A spectacular example of the dissolving effect of roots is the "converter" plant which takes up selenium from stable and relatively insoluble selenium compounds in the soil (Beath and others, 1939, p. 266). With the death and decay of the plant, the selenium returns to the soil in soluble form and is then available for uptake by other plants that lack the power to dissolve selenium.

Movement into the plant of the cations adsorbed on the outer surface of the root tip is controlled by a selective restraining effect of the cell membranes. Some ions are freely admitted and others are impeded to a greater or lesser degree, an effect that is apparently due largely to the pH of the cell sap within the root tip. Lead, for example, is an element that is apparently largely immobilized by precipitation in the cell walls and nuclei of the roots of some plants (Hammett, 1928). Thus, toxic excesses of lead may not reach the active centers of growth in the upper parts of the plant. If the quantity of lead in the nutrient solution is too great, however, the precipitate apparently impedes the flow of solutions and the plant does not grow normally. Uranium and vanadium, elements which are also toxic, are apparently precipitated in the roots in the same way (Cannon, 1952).

Plant nutrition.—The movement of mineral matter within plants is controlled by many factors including free and restrained diffusion, movement of the solvent, electrical and thermal effects, exchange reactions, and, perhaps most important, metabolic accumulation of mineral nutrients in the building of metallo-organic molecules (Broyer, 1947). Of the last type of reaction, the entrance of magnesium into the chlorophyll molecule is a classic example. Many other elements play a similar dominant role as components of enzymes and other catalysts that speed the many vital reactions in a growing plant.

Stated in a different way, the acceptance of inorganic salts into the circulatory systems of plants, and the distribution of those salts throughout the plant structure is a response to the plant's nutritional requirements. In the upper part of the plant, the nutritive elements are commonly enriched in the actively growing cells, particularly in the seed structures and growing tips. As the cells mature, the concentration of these elements declines. There is abundant evidence that the distribution of nutrient elements changes with changing requirements and that the circulatory systems of plants maintain a dynamic balance whereby inorganic material can be not only supplied to fulfill the nutritive needs but also removed when it is no longer needed. Each species of plant has its own individual nutritive requirements that differ somewhat from those of every other species. The nutritive or toxic effect of any one element may depend on the over-all composition of the nutrient solution. The uptake of one element in a plant thus may be suppressed or stimulated by the presence of other elements in the solution (Evans and others, 1951; Ahmed and Twyman, 1953). The composition of plant organs has also been correlated with age of the plant, exposure to sunlight, and height above the ground.

For whatever reasons the elements are needed by plants, it has been definitely established that in addition to the common nutritive elements—potassium, nitrogen, calcium, and phosphorus—most plants require small quantities of many minor elements, including copper, zinc, iron, molybdenum, manganese, sulfur, and boron. If the nutrient solutions do not provide adequate quantities of these elements to the root system, the plant will be unhealthy or may not survive. Some workers have even postulated that plants require a certain small amount of every element in the periodic table, but perhaps in quantities so small that the need could never be demonstrated in greenhouse experiments.

At the other extreme, an excess of any element above a critical level in the nutrient solution will impair the health of the plant or may even kill it. The element here is present in such quantities that it interferes with rather than assists the normal metabolism of the plant and has an over-all toxic rather than a nutritive effect.

For some elements there is an optimum range for the composition of the nutrient solution. If the concentration of an element in the solution is either greater than the upper limit of this range or less than the lower limit, the plant will not grow normally. Boron is perhaps an extreme example; very small quantities are necessary for the growth of many plants, whereas only slightly higher concentrations cause injury. With many plants the range between these two levels is only a few parts per million of boron (Robinson, 1951). For some other elements, such as zinc and arsenic, plants can tolerate a wider range without conspicuous damage. For still others, the existence of either one or both of the limits has not been demonstrated. It is quite possible, however, that further research will eventually show that an optimum range of concentration exists for every element in the supporting solution.

Prospecting by plant analysis.—If the metal content of a sample of plant material is to be useful in prospecting, it should bear a fairly simple correspondence to the metal content of the supporting soil. Considerations of availability in the nutrient solution, together with the many vital and nonvital processes affecting the movement of elements into and through the plant, indicate—correctly— that the correspondence may not be as simple as might be desired. In general, however, if other factors are held constant, a useful degree of correspondence will be found. The problem is to determine what irrelevant factors are most likely to mask the correlation between plant composition and soil composition.

First, the accumulating effect of plants is apparently not a critical factor. In earlier work, this effect was regarded as a highly important mechanism for enriching the metal content of a geochemical sample to a point within the range of sensitivity of the available analytical method. Thyssen (1942) pointed out that the degree of enrichment for each element can be expressed as an "enrichment factor," equal to the ratio of its content in the biosphere to its content in the lithosphere. He suggested that elements characterized by a high enrichment factor are to be recommended for prospecting by plant analysis.

With the high sensitivity of modern analytical methods, an enriched sample is no longer necessary. Furthermore, it has been found that elements that are highly enriched in plant material are not necessarily the ones that will best reflect the relative abundance of that element in the soil. Zinc is an element that may be very highly enriched in many plants. In dwarf birch, for example, the zinc content of the ash of mature twigs is commonly about 1 percent, representing a hundredfold enrichment factor over the 100 ppm zinc of normal soils (Warren and others, 1952b). The variation in the zinc content of most plants, however, is so sensitive to factors completely unrelated to mineralization, such as drainage and sunlight conditions, that the response to differences in the composition of the soil may be largely masked. Recent observations indicate that the content of toxic elements, like uranium and lead, may reflect the composition of the soil more accurately than the nutrient or neutral elements, even though the absolute amount of the toxic element in the plant organ is extremely small. The term "accumulator" plant has been applied indiscriminately to all plants whose chemically determined metal content is useful in prospecting. In view of the dubious significance of the accumulating effect, it is suggested that the use of this term in discussing plant analysis as a prospecting method be discontinued.

The part of the plant selected for analysis is an especially critical factor. As a result of vital processes, the metal content of different organs of the same plant may be widely divergent. Furthermore, the organs of plants differ somewhat in the degree to which their composition reflects the composition of the supporting soil. The zinc and copper content of mature twigs and wood have generally been found to be more stable than the content in immature green tips, leaves, or seed structures in which the variations in composition depend on the rate of metabolism of the actively growing part. The contrast between the metal content of stems and that of leaves or needles collected from the same individuals is illustrated in data collected by Warren, Delavault, and Irish (1952b) and summarized in table 7. The metal content of plant organs can be accurately interpreted in terms of geologic environment, therefore, only where they are based on samples of the same parts of the plant.

Different species of plants take up different amounts of inorganic material from the soil. The contrast in the uptake of copper and zinc by different species all living in essentially the same climatic environment and all growing in unmineralized terrane is also shown in table 7. Here, it would be extremely misleading to attempt geologic interpretations of the metal content of plant samples taken without regard to the identity of the species. In a given environment, a group of species may have similar response to certain elements, and where this can be established it is permissible to include two or perhaps more species in one set of comparable samples.

It is not practical to limit plant sampling to soils of identical pH, drainage conditions, and exposure to sunlight. Variations due to these factors may be minimized, however, by determining the ratio of two elements, such as copper and zinc, whose content in plants responds to nongeologic factors in a similar way. Thus, under normal conditions, a fairly constant copper-to-zinc ratio may be observed even though the absolute amounts of the two elements may vary greatly due to drainage, sunlight, and soil texture. Here a high copper-zinc ratio would indicate copper mineralization of

TABLE 7.—*Average copper and zinc content, in parts per million of dry weight, of leaves or needles, and stems bearing them*

[Compiled from data of Warren, Delavault, and Irish, 1952b]

Species	Copper		Zinc	
	Leaves or needles	Stem	Leaves or needles	Stem
Douglas fir (*Pseudotsuga taxifolia*)	3	5	24	45
Lodgepole pine (*Pinus contorta*)	5	7	37	33
Yellow pine (*Pinus ponderosa*)	4	3	34	29
Whitebark pine (*Pinus albicaulis*)	4	6	27	39
Engelmann spruce (*Picea Engelmanni*)	4	10	41	64
Western red cedar (*Thuja plicata*)	3	2	10	14
Hemlock (*Tsuga heterophylla*)	2	7	12	48
Willow (*Salix sp.*)	12	12	120	120
Aspen (*Populus tremuloides*)	15	11	120	102
Cottonwood (*Populus trichocarpa*)	11	8	130	75
Scrub birch (*Betula glandulosa*)	10	8	170	130
Water birch (*Betula occidentalis*)	11	9	94	110
Mockorange (*Philadelphus lewisii*)	8	7	23	34
Chokecherry (*Prunus demissa*)	10	7	26	36
Saskatoon (*Amelanchier alnifolia*)	11	7	31	30
Mountain maple (*Acer glabrum*)	13	6	31	24
Broombrush (*Symphoricarpos racemosus*)	9	8	24	31
Sagebrush (*Artemisia tridentata*)	17	14	28	20

the bedrock, and an unusually low ratio would similarly indicate zinc mineralization.

Subject to the several modifying factors previously discussed, variations in the chemical composition of the upper parts of the plant correspond to variations in the composition of the solutions tapped by the root system. The roots of many plants extend to considerable depth even in moist climates where water is abundantly available near the surface. The root systems spread out and gather samples from a substantial volume of soil so that the material concentrated in the upper organs is the integrated effect of all the material within a considerable radius. In prospecting, therefore, the metal content of properly chosen samples of vegetation is an indication of the average composition of soil solutions at some depth and to a considerable lateral extent around the sample site. The roots of trees have been seen in tunnels 50 feet below the surface in the uranium mines of the Colorado Plateau. In British Columbia, plant anomalies ranging in width from 4 to 50 times the width of the ore deposit itself have been reported by White (1950). Plant analysis as a method of prospecting is particularly useful in areas of deep transported cover where the ground-water and diffusion patterns do not reach the surface.

Palmqvist and Brundin of the Swedish Prospecting Co. pioneered in the use of plant analysis as a prospecting method by systematically sampling the leaves and needles of vegetation and making spectrographic analyses of the samples reduced to ashes. As a result of this work, they reported discoveries of small tin and tungsten deposits in Cornwall (Swedish Prospecting Co., 1939), a vanadium-bearing shale at Skåne in Sweden, and a tungsten deposit at Yxsjöby in Sweden (Josef Eklund, oral communication, 1948). Electrisk Malmletning, a Swedish geophysical company, has reportedly done some work on the chromium content of vegetation over chromite deposits in Greece, where they found a positive correlation (Josef Eklund, oral communication, 1948). Rankama (1940) conducted a similar investigation of nickel in the ash of birch leaves in the vicinity of known nickel deposits, where by contouring the nickel content of the plant ash he was able to show the location of ore buried beneath 10 feet of glacial cover. Hans Lundberg (oral communication, 1947) used the lead and zinc content of vegetation growing near geophysical anomalies in Newfoundland to determine whether the anomalies warranted drilling for lead-zinc ore. Vogt and Bugge (1943) found that the leaves of dwarf birch growing on covered outcrops of ore contained more copper than other species from the same locality, and also more copper than the same species growing on normal soil.

Beginning in 1945, Warren and coworkers at the University of British Columbia have been active both in research into the biochemistry of copper and zinc in Canadian flora and in the application of plant sampling on a large scale as a prospecting method. They have gathered a vast amount of data to show the normal distribution of copper and zinc in different species of plants and in different organs of the same species (Warren, Delavault, and Irish, 1952b). Guided by these observed relationships, they concluded that stems of 1 full year's growth of gymnosperms, particularly Douglas firs and pines, provide the most useful samples. Using Douglas fir stems, they consider as anomalous a content of more than 9 ppm (dry weight) for copper, more than 60 ppm (dry weight) for zinc, and outside the limits 0.07 to 0.23 for the copper-zinc ratio. They have applied these techniques on a commercial scale throughout Canada and have reportedly uncovered a number of mineralized areas. Warren and his colleagues have also done some experimental work on the distribution of iron, manganese, gold, silver, and molybdenum in plants (Warren, and others, 1952a; Warren and Delavault, 1950a, 1953a).

In the Tri-State lead-zinc district, Harbaugh (1950) found that the zinc content of leaves and twigs of 24 species of trees over mineralized zones were respectively 38 and 25 percent greater than similar samples from barren areas. Twigs of blackjack oak collected within 300 feet of known ore contained 67 percent more zinc than similar samples collected in barren areas some miles distant.

Plant analysis for uranium and vanadium has become an effective method of prospecting for uranium ores in the Colorado Plateau area (Cannon, 1952, 1953, 1954, 1957). The most useful samples come from the twigs and wood of sage, rabbitbrush, piñon, and juniper, which put down their roots to very great depths in search of water. A uranium content greater than 1 ppm on an ash basis indicates geologically favorable ground. It is noteworthy that the 1 ppm threshold for plant ash is less than the 4 ppm normal background for unmineralized rock. Cannon points out that uranium and vanadium are largely precipitated within the root near the point of intake, so that only a relatively small fraction reaches the upper parts of the plant.

Experiments with analysis of plant material have also been reported from California[6], Arizona (Lovering and others, 1950; Warren and others, 1951b), Missouri (Keller, 1949), Michigan (McKinstry, 1948, p. 218), eastern Canada (Riddell, 1952b; Warren and Delavault, 1953b), Poland (Bobrowski and Piechota, 1949), Russia (Tkalich, 1938; Maliuga, 1947), and west Africa (Webb and Millman, 1950).

Prospecting by botanical observations.—The effect of different concentrations of metals in the nutrient solution can go far beyond a simple variation in the composition of the plant organs. High concentrations of metal in the supporting soil may modify the morphology or color of the flora and even determine which species can live under the conditions imposed. Identification of the symptoms and species that are characteristic of the chemical environment thus can provide information that is directly helpful to the prospector without recourse to sampling and chemical analyses of plant material.

The abnormal colors and morphological features of a plant caused by a poisonous element in the nutrient solution are collec-

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[6] Roberts, E. E., 1949, Geochemical and geobotanical prospecting for barium and copper, Stanford Univ., unpublished thesis.

tively referred to as toxicity symptoms. Between the level where a plant can tolerate the concentration of a given element in the soil solutions and the level where it cannot live is a fringe zone where the plant can live but where it suffers from the poisoning effect of the toxic element. Most commonly, the toxemia takes the form of simple stunting of growth. A few plants, however, develop peculiarly diagnostic symptoms that can under favorable conditions be interpreted directly in terms of probable excesses of a toxic element in the soil. Excess quantities of available zinc in soils will cause a yellowing of the leaves or needles known as chlorosis. Somewhat similar chlorotic symptoms have been observed for excesses of copper, cobalt, and cadmium and for a deficiency of available iron (Hewitt, 1953).

The ecological assemblage of plants growing normally in a given environment is a response to the nutritive quality of the soil as well as to the soil texture, drainage, sunlight, and many other factors. Different species of plants have different nutritive requirements. Some grow best in acid soils and others in alkaline soils. Some can tolerate and may prefer deficiencies or excesses of certain elements. The most familiar example of an ecological assemblage characteristic of a particular chemical environment is the flora restricted to limestone soils of high pH. Flora characteristic of acid soils of abnormally low pH have been observed in areas of rock alteration and pyritization (Billings, 1950). A characteristic flora also distinguishes serpentine soils in most climates, although there is some doubt as to whether this is due to the restrictive influence of the abundant nickel, magnesium, and chromium in the soil or to some more indirect reflection of the parent rock. The tolerance of plants for excesses of minor elements also varies with the species. On metal-rich soil, plants with a low tolerance will not survive, leaving the field free of competition to species with high tolerance. In central Africa, search for bare places in the bush caused by excesses of copper in the soil has been used successfully as a prospecting method (Guillemain, 1913; Ball and Shaler, 1914). Vogt (1924a, 1942b) in Norway has observed several plant species thriving on outcrops of cupriferous pyrite to the exclusion of many other common plants, which he explains on the assumption that these species have a high tolerance for copper and hence are left without competitors on the copper-rich soil. Ragweed, which is generally tolerant to heavy metals, is said to grow abundantly on outcrops of zinc ore in Arkansas (Robinson and Edgington, 1945).

Extreme examples of the nutritional response of plants are certain indicator plants that grow exclusively on soil containing an excessive amount of some element. In the Rocky Mountain states, Beath, Gilbert, and Eppson (1939) have shown that a group of plants, chiefly species of *Astragalus,* will grow only on soils containing an excess of selenium. This relationship is so consistent that it is possible to map seleniferous geologic formations by the distribution of the selenium indicators. Inasmuch as selenium-rich forage is highly toxic to sheep and other livestock, the recognition of seleniferous areas by means of the selenium indicator plants is of considerable economic importance. Selenium is also associated with the uranium ores of the Colorado Plateau, where selenium indicators have been used successfully in prospecting for uranium.

Indicator plants for other elements have been reported. In prospecting, the most famous is the calamine violet which thrives only on zinc-rich soils in the zinc districts of Silesia. This species is of only local occurrence. Sulfate indicators have been used in conjunction with the selenium indicators in prospecting on the Colorado Plateau (Cannon, 1957). At the San Manuel copper deposit, California poppies are apparently confined to copper-rich soil, and the population density of this species is closely proportional to the copper content of the soil (Lovering and others, 1950). The distribution of a certain shrub that prefers a soil rich in iron has been useful in determining the extent of the Cerro Bolivar iron deposits in Venezuela (Buck, 1951). Other indicators for copper, lead, zinc, tin, mercury, silver, and gold, have also been reported as useful in local areas (Lidgey, 1897; Dorn, 1937).

The use of indicator plants in mineral exploration undoubtedly has been outstandingly successful in some areas. Such success, however, requires an unusual coincidence of a climatic environment where an indicator plant can thrive, together with the occurrence of ores of the metal to which the plants respond. An appropriate environment for an indicator plant may in reality be a marginal zone for the distribution of that species, where a relatively slight change in conditions will either make the species ubiquitous in its habitat or eliminate it altogether. Thus, although the distribution of the California poppy corresponds with the copper content of the soil at San Manuel, in neighboring areas of slightly different climate the California poppy can grow almost anywhere, whereas in other areas not too far distant it cannot grow at all. No indicator plants can be cited as being universally useful, therefore, and any application of indicator plants to prospecting must be based upon careful preliminary studies of the local flora.

Role of plants in the secondary dispersion cycle.—Plants may play an important part in the over-all movement of elements in the surficial environment. One phase is the decomposition of primary rock-forming minerals. Another is the modification of the mobility of elements, as seen in the action of converter plants on the mobility of selenium. Still another phase is the movement of nutrient solutions from the root tips of plants through the stem and into the leaves, a process that can account for the transfer of substantial amounts of inorganic matter (Goldschmidt, 1937). With the falling of leaves or the death and decay of the plant, the inorganic matter is returned to the surface soil in highly soluble form. A large proportion of these soluble salts is leached by rainwater and removed in the drainage. A part, however, can remain behind as organic complexes and adsorbed ions in the humus and other near-surface horizons of the soil.

The immobilized fraction of the mineral matter brought to the surface by plants can have an important effect in the development of geochemical anomalies in soils, particularly transported soil of glacial or alluvial origin. The subsoil, where iron and alumina tend to be enriched by soil-forming processes, is generally a locus of stable accumulation of metals. Soil samples collected from the *B* horizon may, therefore, show the same pattern of anomalies as the trees overhead. Inasmuch as the immediate source for this enrichment is the decaying humus overlying the subsoil, it is not uncommon to find that anomalous patterns in the *B* horizon of transported soils over ore deposits do not extend downward into the immediately underlying parent material.

STREAMS AND RIVERS

Surface water is by far the most important long-distance carrier of surficial materials. Products of weathering enter the surface drainage in part as solid particles and grains resulting from mechanical erosion and in part as soluble matter. Once this material is caught up in the rapidly flowing water of streams and rivers, it may move in a matter of hours distances that would require days or years in the more sluggish environment of the soil mantle.

Dispersion patterns formed in running surface waters are restricted to drainage channels. The result is an essentially linear distribution of weathering products, as distinguished from the planar pattern resulting from other types of secondary dispersion and the three-dimensional arrangement of most primary dispersion patterns. For this reason, dispersion patterns in drainage systems have been referred to in the Russian investigations as dispersion "trains," in contrast to the halos and other nonlinear patterns formed in the soil cover.

All the products of weathering in a drainage basin must funnel down through the system of streams and rivers that flow out of the area. Thus the load carried by a stream at any given point is a sample of material composited from the area drained by the stream, and its composition will be a reflection of the average chemical composition of the rocks in the drainage basin. Particularly, the metal derived by the weathering of an ore deposit, if that deposit is sufficiently large, may be indicated by a higher than normal metal content of the material being carried away in the drainage water. Under favorable conditions, therefore, chemical analysis of either the soluble or solid load of stream waters can be used in appraising the mineral potentialities of the area drained by the stream.

The characteristic pattern of dispersion of any particular element in a drainage system is dependent on whether it moves as a resistant or stable mineral carried with the solid load of the stream, as an unstable component of the solid load that can readily go into solution with changing conditions, or as soluble matter.

Resistant minerals.—Minerals that do not readily decompose in the surficial environment include both resistant residual minerals inherited from the parent igneous rocks and the clay minerals and secondary oxides that comprise the hydrolysates formed by the weathering of primary minerals. The relative ability of primary minerals to resist decomposition by weathering agencies and the factors governing the formation of stable secondary minerals have already been reviewed in the discussion of weathering products.

Residual minerals commonly make up the bulk of the more coarse-grained fraction of the stream load, which moves primarily by traction, or rolling and bouncing along the streambed at a velocity much lower than that of the water. The clay minerals of the hydrolysate fraction, on the other hand, are commonly fine grained and in turbulently flowing water move in either mechanical or colloidal suspension at the same velocity as the water. When turbulence ceases in lakes and in quieter parts of the stream channel, most of the suspended matter settles out as deposits of mud and silt.

The residual minerals of stream sediments include dominantly quartz, together with a suite of less common, heavier minerals. Near the source, the grain size of the residual minerals is relatively coarse. Transportation of the grains takes place by repeated erosion and resedimentation along the stream bed, during which abrasive forces are continually reducing the size of the grains. Freise (1931) has conducted laboratory experiments to determine the relative rate of disintegration of primary minerals under the abrasive action of flowing water. He arranged the important minerals of placer deposits in the following order of increasing transportation resistance: galena, quartz, zircon, ilmenite, sphalerite, cassiterite, magnetite, wolframite, rutile, chromite, pyrite, and tourmaline. This sequence does not necessarily represent the relative distance the minerals will travel from their source, as no account was taken of the relative rate of chemical decomposition of the minerals or the effect of shape of the mineral grains and the resulting differences in the buoyant effect of running water. By the time the residual minerals reach the larger rivers, even the most resistant of the grains may be reduced to the size of silt particles or smaller and may be carried in suspension along with the clay-mineral fraction.

The continual erosion and redeposition of silt and sand-sized grains can result in a gravity sorting of the minerals, whereby heavier minerals are concentrated in the bottoms of stream channels. Concentrations of this kind, where they contain economically valuable heavy minerals, such as native gold and cassiterite, are known as placer deposits.

Stable secondary minerals under certain conditions can also occur in the coarse-grained fraction of stream sediment along with the more abundant resistant minerals. Chief among these is limonite. Manganese oxides and secondary copper and lead minerals also may be observed in the sand and silt fraction of stream sediments, provided an adequate source of these minerals is present.

The occurrence of certain diagnostic heavy minerals in stream sediments can provide a clue to the distribution of major rock types and to the general geologic setting of the drainage basin. A study of the relative abundance of the heavy minerals in sediments of the James River in Virginia, for example, showed that the mineral assemblage could be correlated with the heavy minerals in the rocks of the areas through which the river flowed, as shown in table 8. Limonite derived from brown iron ores dominates the heavy mineral assemblage in the upper reaches of the river system where it crosses the Valley and Ridge physiographic province. The relative abundance of limonite decreases as the river passes pro-

TABLE 8.—*Heavy minerals of James River sands*

[From Stow, 1939. F, flood; A, abundant; C, common; R, rare]

Minerals	Physiographic provinces Upstream to downstream			
	Valley and Ridge	Blue Ridge	Piedmont	Coastal Plain
Limonite	F	A	C	
Ilmenite and magnetite	C	C	C	A
Zircon	R	R	A	C
Tourmaline	R	R	R	R
Rutile	R	R	R	R
Leucoxene		C	C	R
Hornblende		R	A	C
Epidote		R	C	C
Garnet		R	R	C
Muscovite		C	C	R
Chlorite		C	C	R
Hypersthene		R	R	R
Staurolite			R	C
Andalusite			R	R
Kyanite			R	C
Sillimanite			R	C
Sphene			R	R
Actinolite			R	
Apatite			R	
Biotite			R	
Diopside			R	
Monazite			R	
Tremolite			R	

gressively through the Blue Ridge and Piedmont provinces, and new minerals of local origin appear.

Sampling of heavy minerals in the South Island of New Zealand showed a similar correlation with the geology of the drainage basins (Hutton, 1950). Three geologic provinces were identified, defined respectively by a zircon-scheelite-thorite-uranothorite assemblage, a zircon-garnet-epidote-hornblende assemblage, and a zircon-hyacinth-monazite-xenotime-hornblende assemblage. In this work, the heavy-mineral studies provided an original source of geologic information, as the rocks from which many of the minerals were derived were unknown because of inaccessible terrane.

In prospecting for ore deposits, heavy-mineral studies have been used since prehistoric times. Instead of the heavy accessory minerals of igneous rocks, the prospector looks for heavy minerals derived from the weathering of vein deposits. Many of these minerals occur only in hydrothermal deposits, and rarely or never are found as disseminated accessory minerals. Chief among these are gold, cassiterite, wolframite, scheelite, and cinnabar. The provenance of some of the other heavy minerals, such as platinum, columbite, barite, or pyrite may not be unique, as they can on occasion occur in unmineralized rock as minor accessories as well as in hydrothermal deposits. Thus, cassiterite in a heavy-mineral assemblage is more indicative of economic mineralization in the drainage basin than columbite.

Prospecting by heavy-mineral studies consists in determining the relative amounts of an economic mineral in stream sediments, and in tracing the drainage upstream to the source by following the pattern of increasing concentrations. Techniques of concentrating the heavy fraction and of mineral identification are beyond the scope of this report; they have been described in detail by others (Hutton, 1950; Raeburn and Milner, 1927; Sigov, 1939).

Chemical analysis, rather than mineral identification, may be helpful where abrasion has reduced the grain size to such an extent that the properties of the minerals can no longer be readily observed. Russian workers have made particular use of spectrographic analysis of stream sediments for tin as a method of prospecting for tin-bearing veins in the bedrock (Flerov, 1935, 1938). In the United States, trace analysis of sediments in the dry arroyos below the San Manuel copper deposits in Arizona showed a distribution of copper that could be correlated with the occurrence of ore upstream (Lovering and others, 1950). The copper content of alluvium in the modern streambed was 300 ppm at a point 1.4 miles downstream from the ore outcrop, as compared with a background of 30 ppm. In an ancient alluvial terrace at the same location, the copper content was 140 ppm. Microscopic studies showed that the copper was present in the sediment principally as chrysocolla. The fine-grained fraction of the alluvium contained somewhat more copper than the coarse fraction, probably because of abrasion of the soft chrysocolla as the sediments were washed downstream.

Unstable components of sediments.—Unlike the resistant primary minerals, many of the components of the solid load of streams can go readily into aqueous solution with changing conditions. These unstable components of stream sediments include some fine-grained products of abrasion of residual minerals, unstable chemical or biological precipitates from aqueous solutions, and exchangeable ions.

The relative solubility of finely divided residual minerals is known mainly from inference. Barite, for example, which is a mineral rapidly comminuted by abrasion, might be expected to go into solution readily when present in finely divided form. The same may be true of finely divided cassiterite, which is known from experiment to be measurably soluble in water (Lundberg, 1941). Much has been written on the solubility of finely divided gold, and although opinions differ it would be reasonable to expect that soluble gold complexes could form by reaction of native gold with natural solutions. Except for a few qualitative experiments, however, very little work has been done to determine the fate of fine-grained fragments of residual minerals in stream sediment.

The formation of precipitates in a stream system is most commonly related to changes in pH and Eh, and to biological activity. Iron hydroxide may be precipitated as limonitic coatings on pebbles where acid iron-rich waters derived from the oxidation of sulfates are neutralized in the surficial environment. Traces of many metals may at the same time be removed from solution by coprecipitation with the iron hydroxide. A study of minor elements in an ironstone gravel in Australia, for example, showed that gallium, molybdenum, lead, vanadium, and zinc are concentrated in the limonite (Oertel and Prescott, 1944). Lead in amounts as high as 1 percent was found in the material coating pebbles near the discharge of acid springs in Collar Gulch in the Judith Mountains area of Montana (L. C. Huff, written communication, 1951). A deposit of native copper has been observed in a peat bog near Jefferson City, Mont., where copper-rich water from neighboring mines entered the reducing environment of the peat muck (Forrester, 1942). Lovering (1927), in seeking to explain a similar occurrence of native copper in peat muck, prepared laboratory cultures of the bacteria extracted from the muck. He showed that the reduction of the Cu^{+2} ion to metallic copper was effected by organic compounds resulting from the bacterial metabolism. A large part of the copper in fresh lake waters has been found tied up both in suspended organic matter and in free-floating microorganisms (Riley, 1939). Coatings of manganese oxides on the pebbles in streambeds have been observed in many areas. Ljunggren (1951), for example, reports active formation of manganese-rich pebble coatings in river water containing 0.05 ppm Mn. These reactions are all somewhat reversible. Thus, if for some reason the pH of the environment should change sufficiently, the immobilized material would become unstable, and the contained elements would tend to reenter the aqueous phase.

Exchangeable ions adsorbed to the surfaces of minerals in the finer grained fraction of stream sediments apparently make up the major part of the unstable component of the stream load. By exchange reactions, a balance is established between adsorbed ions and ions in aqueous solution. The content of an exchangeable element in the sediment thus may be an approximate measure of the average content of that element in the stream water. Very little information on the role of exchange reactions with metals in stream sediments has been published. Perhaps the most quantitative study of the problem was by Murata (1939), who found three forms of manganese in a fluvial environment: soluble manganese, exchangeable manganese, and nonexchangeable manganese. The soluble and exchangeable manganese were in apparent equilibrium. The ratio of the exchangeable and the total manganese was related to the intensity of reducing conditions resulting from the decomposition of organic matter, whereby the manganese of insoluble manganese oxides was reduced to form soluble and hence exchangeable manganous ions. Heide (1952) has found that important percentages of many other elements may travel downstream as exchangeable ions attached to the surfaces of fine-grained suspensoids. The notable exceptions are fluorine, chlorine, and bromine, which are not appreciably adsorbed to or otherwise held in the suspensoids. Saito (1951) reports that thorium is more readily adsorbed on suspended matter than radium; thorium is therefore precipitated in coastal waters, whereas radium reaches midocean.

No systematic geochemical prospecting surveys based on determination of the unstable components of stream sediments have been published, although a few writers have observed dispersion patterns in drainage channels that can probably be attributed to this cause. Hawkes (1952) mentions cobalt in the sediments of streams draining mineralized areas in the Blackbird cobalt district of Idaho. White and Allen (1954) found more than 500 ppm copper in the soil of drainage channels below copper-rich dumps at Phoenix Camp, British Columbia. There the copper in the channels was probably precipitated from copper in the waters derived by leaching of the mine dump.

Soluble matter.—The soluble fraction of the stream load travels faster than either the residual minerals or the hydrolysates. Whereas sand- and silt-sized grains and to a lesser extent the clay-sized fraction may remain immobilized for long periods of time as alluvial sediments, the soluble salts move actively with the water. As a result, dispersion patterns of elements dissolved in stream waters are relatively transitory phenomena and are extremely susceptible to sudden changes in both time and space. The principal causes of such variations are: changes in the supply of soluble material at the source, changes along the stream course in the environmental factors governing the solubility of the different elements, and dilution by rain water and tributory streams.

Spring water is the principal source of the soluble salts carried by streams. Changes in the salt content and discharge rate of springs, therefore, will cause corresponding changes in the salt content of the streams fed by them. Major changes in the quantity of soluble material discharged by springs can apparently result from the flushing action of rainwater moving through unsaturated surficial material in which soluble salts have had a chance to accumulate during the preceding period of dry weather. The rising water table resulting from an increase in rainfall may also contribute to the flushing effect. It has been reported that flash-flood waters can, under some conditions, have a higher salinity than waters of the same streams during dry periods. Bryant and Slater (1948) determined the leaching of soluble salts by runoff water in a series of systematic experiments over a year's period. They concluded that

> . . . concentrations of solutes in runoff appeared to be increased by the salts brought to the soil surface by capillarity and evaporation and decreased by downward movement that accompanied infiltration. Because of the vertical movements of soil salts, flash runoffs that followed conditions favorable to capillarity and evaporation were highest in solute concentration. Additional runoff tended to dilute initial runoff and so lower the concentration of solutes, although the total amounts lost were necessarily increased.

A similar direct relationship of solute concentration and discharge rate has been observed for many minor constituents of stream water. The cobalt content of the water of many small streams in the Blackbird cobalt district of Idaho, after an unseasonal August rain, averaged about four times the cobalt content of the same waters measured 2 weeks previously, during a dry spell. The rate of discharge of the streams here was also higher. An increase in the heavy-metal content of streams during rising water level has also been noted by workers in eastern Canada.

Webb and Millman (1950) report an initial decrease in the heavy-metal content of streams draining an area of lead-zinc mineralization in Nigeria after a heavy rain; this was followed by a marked increase in metal content after several days of heavy rainstorms. The initial decrease was ascribed to simple dilution by direct surface runoff and the later increase largely to increments of soluble metal flushed out of the deeper horizons of the soil. These observations differ somewhat from the leaching cycle described by Bryant and Slater (1948), possibly because of differences in climatic effects.

Heide (1952) found, however, that although the iodine content of the Elbe River varied directly with the discharge, the major constituents in the same suite of samples varied inversely. It is difficult to rationalize an opposite behavior of different soluble components of the same water system with a single, simple process, such as leaching of salts by rainwater. Other factors not understood are involved in the process.

Inasmuch as short-term variations in the composition of stream water can apparently result from changes in the weather, several writers (Huff, 1948; Webb and Millman, 1950) have recommended establishing base sampling stations, where the metal content of the water is rechecked periodically and the variations used in deriving a correction factor to be applied to the field data. In this way, it may be possible to reduce the error due to short-term fluctuations with time.

The supply of soluble metals derived from the oxidation of a sulfide deposit depends to a large extent on the rate of oxidation of the deposit. The rate of oxidation varies somewhat with climatic conditions. For example, in the relatively cool climate of the Pacific Northwest, spring water containing 0.005 ppm heavy metal has been considered a promising indication of mineralization (Warren and others, 1951a), whereas in southwestern Wisconsin, spring water flowing from undeveloped sulfide deposits contained as much as 0.05 ppm heavy metal (Kennedy, 1956), and in Nigeria a similar spring was found to contain 0.5 ppm (Webb and Millman, 1950). The rate of oxidation of sulfide material also depends on the accessibility of the material to oxidizing solutions. This effect is especially pronounced where the deposit has been opened up with test pits or underground workings, or where mined ore has been piled on the surface. Thus, an abandoned mine or prospect in which the sulfide material has been exposed to accelerated oxidation may discharge from 10 to 100 times as much soluble metal into the stream water as the same deposit before it had been worked. In previously prospected areas, therefore, the increments of soluble metal derived from undiscovered deposits may be completely masked by the contribution from the known prospects. Water analysis for this reason may be more useful in locating forgotten prospects than in finding new prospects.

Changes in the chemical and physical environment can modify the composition of surface waters by changing the mobility of some elements. The elements most sensitive to changes of this kind are the ones of intermediate mobility. The extremely mobile ions, such as sodium and sulfate, will not be precipitated by any normal variation in the environment. At the other end of the mobility scale, the extremely immobile elements such as chromium will remain in the solid phase throughout the normal cycle. Many intermediate elements, however, including copper and zinc, are very sensitive to changes in pH, the nutritive requirements of plant life, organic complexing agents, and the exchange capacity of bottom sediments, to mention a few of the disturbing factors. These effects can vary in both time and space.

Of the factors causing a time variation, perhaps biological activity has the most pronounced effect. Heide (1952) has noted that the nitrate content of the Elbe River is inversely related to the temperature of the water. He ascribes this to the increased metabolism of organisms in a warm environment with a resulting increased removal of nitrates for nutritive purposes. Riley (1939), in following the biochemical cycle of copper in a lake in Connecticut, found that in the autumn the copper content of some stream waters increased by a factor of 10 when the copper was released by the decay of fresh plant litter.

Of the factors causing a variation in space, removal of ions by progressive adsorption to the solid suspensoids and sediments in the stream appears to play an important role. Many workers have noted a rapid decrease in the metal content of stream water in passing downstream from an area of high metal discharge.

For example, Warren, Delavault, and Irish (1951a, p. 616) report that "... in a very short distance it is possible for a stream to lose its metal content, although the stream as a whole may exhibit no change in volume." L. C. Huff (written communication, 1954), in measuring the metal content of water draining mine workings at Jerome, Ariz., noted that the zinc content fell off by a factor of 25 in flowing 3 miles through an irrigation canal, with no water entering the canal to cause dilution and no change in pH (table 9). Dilution, of course, cannot account for a decrease in metal content of this kind. The most probable explanation is a progressive removal of metallic ions by exchange reactions, together with perhaps some removal by biological activity.

A variation in pH, particularly in acid waters issuing directly from an oxidizing sulfide mass, can cause major variations in the metal content of the water. Copper tends to be removed from solution as the pH rises above 5. Thus copper-rich acid waters, as they are progressively diluted and neutralized in flowing down-

TABLE 9.—*Heavy metal content of water from irrigation ditch draining the U.V.X. mine, Jerome, Ariz.*

[Samples collected and analyzed by L. C. Huff]

Distance from mouth of tunnel (miles)	pH	Heavy metal (ppm)	Distance from mouth of tunnel (miles)	pH	Heavy metal (ppm)
0	8.0	2.0	1.8	--------	0.4
.3	--------	1.2	2.4	--------	.08
.9	--------	.6	3.2	--------	.08
1.4	--------	.5	3.5	8.0	.06

stream, will lose much of their copper content. This effect may be seen in the data on the copper content of the drainage below the mines at Butte, Mont., collected by Huff (written communication, 1947) as shown in table 10. Here, if it is assumed that the zinc content falls off by a simple factor of dilution, the copper-zinc ratio will be a measure of the tendency of the copper to remain in solution. It is notable that the ratio remains constant until the pH exceeds 5.0 and then falls off rapidly, indicating that copper joins the solid load of the stream in some form.

TABLE 10.—*Metal content of water in drainage from copper mines at Butte, Mont.*

[Samples collected by L. C. Huff; analyses by Norman Davidson and L. C. Huff]

Stream	Distance below mines (miles)	pH	Parts per million			Cu:Zn ratio
			Cu	Zn	Fe	
Silverbow Creek	2	4.5	70	400	80	0.17
Do	6	4.8	20	150	30	.13
Do	12	4.8	15	100	11	.15
Do	18	5.0	10	80	2.5	.12
Deer Lodge River	27	5.8	.5	25	.8	.02
Do	41	5.8	.08	10	.4	.008
Clark Fork River	82	5.8	.05	3	.8	.016

Dilution of a stream by increments of water from tributaries of different composition generally has a simple arithmetic effect, provided the turbulence is adequate to cause complete mixing over a short distance, and provided of course that no chemical reaction between the two waters causes a precipitate to form. With larger streams and rivers, where laminar rather than turbulent flow predominates, many miles may be required for complete mixing of water of contrasting compositions. For example, the chloride content of water from the left bank of the Elbe, just below the confluence of the chloride-rich Saale River, is 17 times higher than that on the right bank; 27 kilometers below the confluence, the chloride content of water from the left bank of the Elbe is still three times higher than that from the right bank (Heide, 1952). In sampling the water of larger rivers, therefore, care should be taken either to obtain a true average sample composited from subsamples taken across the full width of the river or to collect and analyze separate samples from the two sides of the channel.

Prospecting methods based on chemical analysis of stream water have been investigated by many workers. The heavy-metal content of waters has been most widely used, probably because of the simplicity of the dithizone method of analysis (Sergeev, 1946a; Huff, 1948; Sokoloff, 1948; Webb and Millman, 1950; Riddell, 1952a; Ohashi, 1952; Shima, 1953b, 1953c, 1953d, 1953e; Hayashi, and others, 1951). Work has also been done on copper alone (Vogt and Rosenqvist, 1943), gold (Konovalov, 1941), iron (Kimura, and others, 1950, 1951; Shima, 1953c, 1953f), manganese (Shima, 1953a, 1953c), and sulfate (Hayashi, and others, 1951; Kimura, and others, 1950, 1951; Shima, 1953f).

In tracing the dispersion train of an element in a drainage pattern, especially careful consideration must be given to the form in which the metal or other element is transported. A dynamic equilibrium exists between the unstable fraction of the solid load of streams and the soluble fraction. Whether the bulk of any particular element is traveling in the solid or the soluble fraction at any point in the drainage system depends on the balance of many factors that may be difficult to evaluate on the basis of theory alone. In any given set of field conditions, however, it should be possible to get at least an empirical idea of the partition of an element by carrying out determinations respectively of the total content of the element in sediments, the fraction readily extractable from sediments in weak reagents, and the soluble salts. The best material to be sampled in any reconnaissance exploration program and the most suitable analytical method can then be selected on the basis of this preliminary information.

LAKES

Fresh-water lakes may be considered temporary resting places during the transportation of weathering products, where the rapid movement of stream and river water gives way to a quiet environment dominated by sedimentation and biological activity. The bulk of the solid fraction of the stream load is dropped at the inlets. Some of the soluble components of the streams entering a lake may enter the biological cycle of fresh-water organisms and be deposited with the organic sediment that accumulates in the lake bottom. Copper in particular is known to be immobilized in this way (Riley, 1939; Nichols and others, 1946).

Soluble metals originating from the weathering of ore deposits also may be trapped in the bottom sediments of lakes. Vogt (1942c) describes lake deposits of bog manganese ore containing traces of zinc, copper, nickel, and cobalt derived from sulfide bodies in the tributary basins.

In addition to the metal introduced by streams flowing into a lake, some water can enter lakes directly by seepage of ground water around the shores. Chisholm (1950a) describes lake water collected offshore from a known mineralized vein, where he found that readily detectable amounts of heavy metals occurred within 5 feet of the shore. The heavy-metal content dropped rapidly more than 5 feet from the shore and in the absence of nearshore mineralized zones, the metal content of the water was negligible. This metal undoubtedly came into the lake from seepages of metal-rich ground water.

MARINE BASINS

Deposition of sediments brought into marine basins by rivers is the final phase of the surficial geochemical cycle. On entering a body of salt water, most of the minor elements dissolved in river waters are precipitated and deposited along with the sediments (Krauskopf, 1952). The material deposited is a sample of the terrane drained by the rivers that flow into the basin. The chemical peculiarities of some sedimentary rocks have been explained on the assumption of similar peculiarities in the rocks of tributary land areas. For example, the Lockport dolomite of the Great Lakes area and the Mansfeld shale of Germany are unusually rich in base metals that are presumed to be syngenetic. These metals may have originated from the weathering of a terrane particularly rich in those metals.

In addition to the material brought into marine basins by rivers, a small contribution may also be received from rocks cropping out on the floor of the basin. Huff (1955) has correlated the copper content of the basal sandstone of Cambrian age in the Jerome area of Arizona with copper ore in the Precambrian rock floor of the sea during earliest Cambrian time. An oval-shaped area of sandstone containing more than 100 ppm copper extends for as much as 2 miles around the exposure of Precambrian rocks of the

United Verde ore body. Background copper content is less than 50 ppm. This pattern is interpreted as the result of lateral dispersion of copper by water currents and waves washing back and forth over copper ore exposed in the floor of the shallow marine basins.

APPLIED GEOCHEMICAL PROSPECTING

In the preceding pages some of the laws governing the dispersion of the chemical elements in earth materials and the characteristics of the resulting dispersion patterns have been reviewed. The application of dispersion-pattern studies to practical problems of mineral exploration remains to be considered. After a review of the historical development of geochemical methods of prospecting, some comments are made on the selection of the most appropriate exploration method and on techniques of carrying out a geochemical survey.

HISTORICAL SKETCH

Early development. — The basic principle upon which geochemical prospecting is based—the following of dispersion patterns—has probably been recognized and used since man first began his search for metal. The ancient prospector who panned gold upstream in quest of the mother lode or examined outcrops and stream beds for iron stains was looking for the same types of clues to buried ore as the modern prospector with his kit of chemical tests. The chief difference was in the use of mineralogical observations rather than chemical analyses.

Probably the first written record of the use of chemical analyses in prospecting is in Vannoccio Biringuccio's "Pirotechnia," (Biringuccio, 1540, p. 15) published in Venice in 1540, in which he says:

> There are some who praise highly as a good sign certain residues that waters make where they are still, and after having stood for several days, frequently warmed by the rays of the sun, they show in some parts of their residues various tinctures of metallic substances. There are others who usually take this water and cause it to evaporate or dry up entirely by boiling it in a vessel of earthenware, glass, or some other material, and they test the gross earthy substance that remains at the bottom by testing, by the ordinary fire assay, or in some other way that pleases them. In this way (although they do not have an exact proof) they approach some sort of knowledge of the thing.

During the 40-year period before 1935, many authors both on this continent and abroad have reported observations on the response of vegetation to underlying ore (Lidgey, 1897; Lungwitz, 1900; and references in Dorn, 1937), and on the distribution of traces of metals in rocks associated with ores (Vogt, 1923; C. H. White, 1924; Wilson, 1935). They were the results of isolated projects, however, and did not represent large-scale or concerted research programs.

Russia.—The first large-scale systematic investigation of chemical analysis as a method of prospecting was undertaken in 1932 by Soviet geologists (Fersman, 1939; Sergeev, 1941). By 1935, the geological staff of the Central Geological and Prospecting Institute in Moscow had perfected spectrographic analytical equipment and sampling procedures suitable for routine geochemical soil surveys. Three field projects were undertaken in 1935, 8 in 1936, 6 in 1937, and 3 in 1938. Seven of these projects depended upon semiquantitative spectrographic analyses of soil and stream sediment for tin, a procedure referred to in the Russian investigations as the "stannometric survey." The remainder of the Russian projects during this period were orientation and prospecting surveys for copper, lead, zinc, nickel, chromium, tungsten, molybdenum, and borates. Most of this work was based on spectrographic methods of analysis, although spot tests, flame tests, and colorimetry were used in a few projects. In the course of these surveys a total of more than 45,000 samples were collected and analyzed. Well-defined chemical indications associated with known ore were obtained in all but 3 of the 20 areas investigated, and 5 new mineral discoveries were reported. In addition to the discoveries, many geochemical anomalies were found which had not been confirmed by subsequent exploration at the time of the last comprehensive report (Sergeev, 1941) received in the United States.

Much of the analytical work in connection with these surveys was done in the field or in temporary field headquarters. A small spectrograph with a portable power supply was constructed for use under primitive conditions in the immediate vicinity of field operations (Ratsbaum, 1939). This unit could be disassembled for transportation by truck or where necessary by pack animals.

In addition to the soil work, some experiments have been carried out in the Soviet Union with analysis of vegetation as a prospecting method (Tkalich, 1938; Maliuga, 1947); to date, no report of large-scale prospecting activity based on plant sampling has been received. It is perhaps worth noting that the publication date of the paper by Tkalich antedates the earliest Scandinavian reports on plant surveys by about a year. Preliminary investigations of the metal content of surface water in relation to mineralization have also been reported from the Soviet Union (Sergeev, 1946a).

Scandinavia.—In 1936, Palmqvist and Brundin of the Swedish Prospecting Co. undertook experiments with spectrographic analysis of plant ash as a method of prospecting. Trial geochemical plant surveys in Cornwall and Wales indicated abnormally high contents of tin, tungsten, lead, and zinc in the leaves of trees and shrubs growing over soils containing correspondingly large proportions of those metals (Swedish Prospecting Co., 1939). On the basis of these experiments, a patent (Brundin, 1939) was obtained to cover systematic sampling of plant material followed by spectrographic analysis of the plant ash as a method of prospecting. For several years, the Swedish Prospecting Co. conducted geochemical surveys in conjunction with its regular geophysical service to the mining industry, and many areas were systematically prospected by plant analysis. Because of the confidential nature of the exploration contracts, very little of the results of this work have been published. The company was dissolved during the early years of the war, and large-scale geochemical prospecting work in Sweden has not been resumed.

In 1939, Rankama (1940) made an experimental study of the nickel content of plant samples from a number of nickel deposits in the glaciated country of northern Finland. Within the last few years, additional experiments with geochemical dispersion patterns related to ore have been undertaken under the auspices of the University of Helsinki (Marmo, 1953) and the Geological Museum (Salmi, 1950).

Beginning in 1938, Vogt and coworkers at the Technical University of Norway have investigated the dispersion of weathering products of known sulfide deposits in soil, vegetation, and surface water, and have published a series of papers summarizing their results. (See Vogt and also Rosenqvist and Vogt).

Canada.—In 1939 and 1940, Lundberg (1941), following the lead of the Swedish investigators, experimented with spectrographic analysis of vegetation for lead as a prospecting method. Tests were carried out at Buchans, Newfoundland, and at several other localities in eastern Canada. Although the results were generally promising, Lundberg's work was suspended because of wartime restrictions, and has not been resumed.

In 1945, H. V. Warren and his coworkers at the University of British Columbia undertook a research program on the metal content of vegetation as a method of prospecting and a few years later began applying the methods on a large scale to practical prospecting problems. (See references under Warren and others). This program has been maintained actively to the present time.

Widespread Canadian interest in all methods of geochemical prospecting has been growing rapidly since about 1950 and has resulted in the publication of reports by many independent investigators (Chisholm, 1950a, 1950b; Bischoff, 1954; Riddell, 1950, 1952a, 1952b, 1954; White, 1950; White and Allen, 1954). An increasing number of Canadian mining companies and private consulting groups have organized their own geochemical prospecting units and, using primarily geochemical soil surveys, have had very successful results in integrating the geochemical work with their other exploration activities.

United States.—Before the end of World War II, geochemical prospecting work in the United States was relatively sporadic (Campbell, 1941; Fowler, 1950; Jakosky and others, 1942). Large-scale experimental work in the United States was begun in 1946 with the initiation of geochemical prospecting research by the U. S. Geological Survey. Part of this program was directed toward developing chemical tests suitable for geochemical prospecting work and has resulted in the publication of rapid procedures for the determination of most of the ore metals (Lakin and others, 1952; U. S. Geological Survey[7]). The remainder of the program was concentrated principally on experimental sampling surveys under a wide variety of geologic and climatic conditions to determine the characteristics of dispersion patterns of metals in rock, residual soil, vegetation, and natural water. (See reports by Cannon, Cooper, Hawkes, Huff, Kennedy, Lovering, and Morris in Literature Cited.) The Geological Survey program is being continued actively at the present time under the direction of T. S. Lovering.

In addition to the Geological Survey's program, many experimental projects have been carried out by independent workers (Graf and Kerr, 1950; Harbaugh, 1950; Keller, 1949; Nackowski, 1952).[8]

Geochemical methods have been applied by many of the large mining companies to their exploration problems, particularly in the southern Appalachians and in the Pacific Northwest, with favorable results. Descriptions of some of this work have been published (Fulton, 1950; Gilbert, 1951, 1953; Kingman, 1951). This represents only a minute fraction of the total amount of work done, as very little information on the results of geochemical surveys by American mining interests has been released to the public. Recent progress in the United States on the development

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[7] U. S. Geological Survey, 1953, Additional field methods used in geochemical prospecting by the U. S. Geological Survey: U. S. Geol. Survey open-file rept.

[8] See also footnote 3 on p. 242 and footnote 6 on p. 297.

and application of geochemical prospecting methods has been summarized by Webb (1953).

Africa.—In 1949, Roberts (1953) working in Nigeria carried out the first experiments with geochemical soil surveys in tropical terrane. Roberts' work was followed by further experiments in the same areas of Nigeria by Webb and Millman (1950, 1951) and Hawkes (1954). Beginning about 1952, several of the large mining companies undertook experimental soil sampling programs in Rhodesia and Tanganyika, many of which are still in progress.

Japan.—Under the direction of Professor Kenjiro Kimura of the Department of Chemistry at the University of Tokyo, chemical tests were developed for the determination of copper, zinc, iron, manganese, and sulfates in water and for copper, zinc, lead, silver, nickel, manganese, cobalt, and sulfate in soils and rocks. Experiments in the vicinity of known Japanese deposits showed favorable results, and Kimura's methods are now in current use by the majority of Japanese mining companies. A very large number of articles have appeared in Japanese publications. (See reports by Kimura, Shima, Fujihara, Hayashi, Ohashi, and Umemoto in Literature Cited). They are almost entirely in the Japanese language, and very few of them have been translated or otherwise made accessible to non-Japanese workers. Thus, at present, it is not possible to comment on either the scope or success of this work.

Other countries.—Work in Australia began in 1948 with experimental investigations by Sokoloff (1949, 1950a, 1950b, 1950c, 1951a, 1951b), and is currently being continued under the auspices of the government and private mining interests (Engineering and Mining Journal, 1953). A broad program of research on the application of geochemical prospecting methods to problems throughout the British Commonwealth is currently being conducted with government sponsorship under the direction of J. S. Webb at the Imperial College in London (Williams, 1954). A government-sponsored program has also been started in India. In Yugoslavia, research work on the relation of the composition of spring water to the age of faults and to geochemical provinces has been reported by Miholić (1948, 1949). Papers on geochemical prospecting have also been published by workers in Germany (Fricke, 1953), Italy (Minguzzi and Vergnano, 1948), Poland (Gaweł, 1947; Bobrowski and Piechota, 1949), and Portugal (Neiva, 1949).

CHOICE OF EXPLORATION METHODS

Mineral exploration may be considered the search for a target, on which the bull's-eye is the ore deposit. Just as the center of the marksman's target is surrounded by concentric rings, so most ore deposits are closely related to a series of larger target areas, each characterized by some physical or chemical feature that is diagnostic of the ore environment. Some of these features, such as favorable host rocks or geologic structures, are related to the genesis and localization of the ore. Others, such as geophysical anomalies, are a direct response to some unusual property of the ore body itself. Still others, as for example the pattern of metals dispersed in surficial material near the ore, result from the breakdown of ore minerals by agencies of weathering. Each geologic, geophysical, and geochemical feature of the environment of an ore deposit defines a target area of characteristic size, shape, and relationship to the ore.

Some characteristics of the ore environment extend over large areas and form targets that are useful in broad-scale reconnaissance. Others are restricted to the immediate vicinity of the ore body and are of most value in detailed exploration. On entering a new field, the exploration geologist may make a reconnaissance geologic study, looking for regional criteria for mineral deposits to help him decide which parts of his territory show the best chances for the occurrence of ore and which other parts can be eliminated as relatively unfavorable. When he has selected regions that appear to be promising, he may then examine the geologic features within these large tracts in more detail using more restricted aspects of the ore environment to determine where intensive exploration is desirable. This process of elimination of unfavorable areas and of increasingly intensive study of the favorable areas is continued step by step up to the ultimate proving of the deposit by drilling and underground exploration. It is a process of progressively reducing the size of the target, where at each step the target is the area having the highest probability of containing ore.

The traditional prospector, before the days of modern exploration aids and modern concepts of economic geology, was guided to the target mainly by the distribution of known deposits, plus a liberal amount of intuition. His next step was the tedious examination of every bedrock exposure for signs of mineral deposits. This was a job for a very patient man, for whom time had little value. Furthermore, he was almost entirely restricted in his chances of success to deposits that were exposed at the surface; hidden ore could be found only by the rarest accident. As a result of the conscientious work of prospectors of an earlier generation, very few major ore deposits remain to be found by simple outcrop surveys.

The well-trained modern prospector, however, has a wide choice of methods of reducing his target area, both in the reconnaissance and in the detailed phases of his search. His selections of promising areas can be guided not only by the distribution pattern of known mines and prospects but also by considerations of favorable geologic structures, host rocks, and alteration patterns. His direct geologic observations can be reinforced and augmented by geophysical data, which will tell him not only more about the geologic setting, but will in many areas provide indications of the ore itself. Every method he uses in narrowing the target area increases the probability of success of the final and most expensive phase of exploration, the diamond drilling and underground exploration. The alert geologist is, therefore, ready to use any set of reliable criteria available to him as additional sources of evidence.

The choice of an exploration method should be guided by a consideration of size of target, probability of locating target, expected value of the ore deposit to be found, and cost per unit area for making the survey.

By size of target is meant the size of the favorable area that can be delimited by the method in question. Examination of regional structural trends on a geologic map of the United States, for example, may show that the Appalachian belt is a favorable area for mineralization. This presents a large target. Airborne magnetic surveys, on the other hand, will not indicate a magnetic anomaly much more than 1,000 feet from the magnetic body responsible for the anomaly, and ground magnetic observations must be made usually within 100 feet of the magnetic body to detect it. These are small targets.

The probability of locating a target means the probability of obtaining and recognizing indications of an ore body or mineralized district by the method being used. It depends on whether a target exists and, if so, how effective the exploration method is in locating it. A zinc deposit containing only the nonconducting mineral sphalerite is not likely to have an associated resistivity target; no method depending on resistivity could be expected to find it and the chances of finding a target are, therefore, extremely small. On the other hand, geochemical soil anomalies are present over virtually all base-metal deposits that are covered only by residual soil. Here the chances of finding a target are excellent if the survey is properly conducted.

The expected value of ores to be found in a given area can be determined by consideration of the value of known deposits in the area, or, if no deposits have been discovered, by comparison with geologically similar areas where important deposits are known to occur.

The cost of the prospecting survey is the only one of the critical factors that can be computed quantitatively. It is important, however, to compare costs on a unit-area basis. High total cost does not necessarily imply a high unit-area cost. Airborne geophysical surveys, therefore, although they represent a high cost of overhead and hourly operation, are relatively inexpensive when computed in terms of cost per square mile.

The efficiency of any exploration method—whether geologic, geophysical, or geochemical—will depend on the balance of these four factors. Thus low cost of making the survey (airborne magnetic, for example) can offset small target size, poor chances of finding a target, or a low probability for the occurrence of large ore bodies. Conversely, a high-cost survey such as geochemical soil sampling is justified if large ore bodies are expected, and there is relatively little chance of passing by a deposit if one occurs in the area of the survey.

It should be apparent from the foregoing discussion that geochemical methods of mineral exploration have no unique claim to universal applicability. For any given problem, the pros and cons of any geochemical method must be weighed against those of the other available prospecting methods and a proper place assigned to each in the schedule of reducing the target size.

PRELIMINARY ORIENTATION

Although the past record of effectiveness of geochemical prospecting methods is certainly helpful in planning exploration in a new area, there is no substitute for a preliminary orientation survey to determine which methods will work in the particular area under study. No two field problems are exactly alike. Unexpected factors may locally modify the dispersion patterns of ore metals and make them difficult or impossible to use as indications of buried ore.

The cost of a geochemical survey can also be estimated by preliminary experiments. If geochemical methods are to be economically feasible, techniques of field sampling and chemical analysis must be both simple and cheap, so that the routine work of carrying out a geochemical survey can be entrusted to relatively low-cost personnel. Quantitative accuracy may be sacrificed for the sake of greater productivity as long as the methods are still adequate to locate the significant anomalies. In applied prospecting work, the aim is to find ore bodies rather than to make accurate geochemical maps. Many interfering and disturbing factors can be ignored under certain conditions if experience shows that they do not materially alter the geochemical trail that is being followed. Whether or not they actually can be ignored in a particular exploration problem is a question that can only be answered by preliminary orientation surveys.

Orientation surveys in the vicinity of known ore are, in the writer's opinion, mandatory if any degree of success is to be expected from a geochemical survey. If possible, the experimental surveys should be conducted in the vicinity of deposits that have not been disturbed by previous exploratory work, so that the natural geochemical pattern as it existed before the advent of man can be observed. Many expensive sampling programs have failed either because the type of anomaly being sought did not exist in the area or because the samples were taken in the wrong places or of the wrong material. Many geochemical surveys were successful insofar as they served to delineate the anomalies, but they were so expensive and laborious as to be wholly uneconomic as a practical method of prospecting. In either case, preliminary work would have shown not only what kinds of anomalies could be expected but also what shortcuts could have been taken to eliminate unnecessary precautions and refinements. All practical exploratory work should be guided by the principle that the least expensive method of finding the ore body is the best.

LAYOUT OF SAMPLING PROGRAM

Two questions that must be answered before embarking on a geochemical survey are: what will be the most effective geometric pattern for sampling, and what is the maximum permissible spacing of samples. Both can be answered with preliminary experiments.

Sample pattern.—Sampling of any material on a regional basis is not only easier but commonly more effective if it is laid out on a simple geometric pattern. In geochemical surveying, sample patterns should be made to fit the geometry of the expected anomalies. Most geochemical anomalies are the result of movement either through well-defined channels (dispersion trains), spreading predominantly to one side of the source (dispersion fans), or spreading upward or outward in all directions from the source (dispersion halos). Different sample patterns are needed for the most efficient delineation of anomalies of these different shapes.

The dispersion trains developed by flowing stream water assume a linear form determined by the drainage channels. Reconnaissance geochemical work based upon the following of dispersion trains consists simply of collecting and analyzing samples from the larger streams; where the analytical data show an anomalous metal content, the trail of increasing metal content is followed upstream to the source. The maximum size of stream that will give a sure geochemical indication of mineralized zones in the drainage basin cannot generally be determined in advance without preliminary experimental sampling downstream from known but undisturbed deposits. The pattern of sampling to be followed in tracing an anomaly upstream is fixed by the pattern of tributaries entering the main stream. Sergeev (1946a) suggests a system of collecting three samples at each important confluence, two in the main stream respectively below and above the tributary, and one in the tributary itself. In practical work, it may be more convenient to sample the main stream at fixed intervals and to double back if the metal content falls off sharply in going upstream. In following dispersion trains, it is particularly desirable to have analytical methods that can be used on the spot.

Fan-shaped patterns are formed by glacial movement and by creep of surficial material down steep slopes. Generally, the concentration of metal in a fan apexing at an ore deposit decreases with distance from the source. Traverses designed to find dispersion fans with the least effort should be laid out at right angles to the direction of movement. Particularly on steep slopes, soil-sample traverses parallel to the contours and transverse to the direction of slope movement have been recommended (Sergeev, 1941).

Dispersion halos due to spreading of material in all directions from a small source make up most of the anomalies found in sampling residual soil and vegetation. A perfectly equidimensional halo can best be located by means of an equal-spaced spread of sample points. The shape of the halo, however, is rarely equidimensional, as it commonly mirrors to some extent the shape of the source. Most ore deposits are tabular, and the elongate pattern of the resulting anomalies in the overlying cover can be mapped most effectively by collecting samples of soil and plants along parallel traverse lines crossing the ore structure at right angles. Traverse lines are commonly spaced at intervals of not more than one-half the strike length of the anticipated mineralized zones. This spacing permits at least one and usually two lines to intersect every important anomaly. Thus if a deposit must be at least 1,000 feet in strike length to be of economic interest, a traverse spacing of 500 feet should be recommended.

One weakness of parallel sample traverses in soil and plant surveys is that samples from ridge crests, slopes of varying degrees of steepness, and valley bottoms, each subject to somewhat different interpretation, all appear on the same map. On ridge crests, the residual soil reflects the composition of the bedrock almost directly beneath, whereas on slopes, because of creep or landslide effects, it may reflect bedrock occurring a certain unknown distance upslope. Where distortion of this kind becomes a serious problem, it may be desirable to lay out reconnaissance soil or plant traverses to conform with the topography rather than with a rigid, rectilinear system of coordinates. Topographically controlled sample patterns may be laid out along the crests and spurs of ridges, down the slope at right angles to contours, on hillsides parallel to contours, or on hillsides parallel to the ridge crest.

Where the strike of the mineralized structure is not known, it may be desirable to lay out an equal-spaced checkerboard pattern of samples. Here the spacing should be close enough that at least two and preferably three or four samples will fall within any anomaly that reflects a deposit large enough to be of economic interest.

Some geochemical anomalies do not fit the convenient classification of trains, fans, and halos. For these the most suitable sample pattern may be selected by considering the geometry peculiar to the anomaly. In most cases this is fairly obvious. If a geochemical province is manifested by the composition of diabase dikes, then diabase dikes should be sampled. Similarly, wells, springs, and seepages should be sampled if a ground-water pattern is sought. Sampling here must be guided by the distribution of the material sampled and cannot be laid out on a previously established geometrical grid.

Sample spacing.—The spacing of samples should be close enough so that no important anomaly could normally be overlooked, but no closer. If the anomaly is inhomogeneous, so that a proportion of the samples taken within an anomalous area will fail to indicate the anomaly, correspondingly more samples will be necessary than if the anomalous values are distributed uniformly. Also, if erratic high values of no economic significance occur outside the anomalous area, a closer spacing of samples will be called for. Here, a great deal depends on whether or not the analytical data are reported promptly, so that isolated anomalous values can be checked by local detailed work before the sampling party leaves the area. If so, it may be safe to use a wider spacing for the initial survey and to plan on immediate rechecking of all anomalous spots with detailed grids.

The above comments apply to any prospecting method involving systematic measurements or observations. More specifically, experience in most areas has shown that in sampling residual soil and plants, a spacing of 100 feet is both adequate and necessary. Anomalies in soils developed by ground-water movement are likely to be more restricted in area, requiring a spacing of from 10 to 50 feet. In glacial soils, a spacing of as much as 500 feet may be effective in locating glacially dispersed patterns. Still larger targets, as for example in a stream system where an anomalous metal content can be detected perhaps 10 miles from the source, can be sampled on a correspondingly wider spread.

SAMPLING TECHNIQUES

The technique of collecting samples will naturally depend on what is being sampled, whether rock, soil, vegetation, water, or stream sediment.

Rock.—Elements occurring in rocks as primary dispersion patterns may be either evenly disseminated throughout the rock mass or segregated as clots or swarms of minute fracture fillings. If it can be established that the rock is relatively homogeneous, single grab samples may suffice. If the composition is spotty and erratic, however, it is safer to collect either channel samples or chip samples composited along sections of traverse as described by Cooper and Huff (1951). Split diamond-drill core is also suitable. The size of sample should be governed by the relative homogeneity of the material, a factor that can be determined by preliminary experiments. Ten grams is adequate for most analytical methods. Cloth sacks and cylindrical ice-cream cartons are suitable as containers for rock samples.

In working with primary dispersion patterns, it is well to remember that the distribution of metals in residual soils may reflect the general pattern of the primary anomaly in the parent rock fairly accurately. In fact, the averaging effect resulting from weathering and soil formation may serve to give a more homogeneous primary pattern than channel sampling of the rock itself. Soil samples can be collected and analyzed more economically than rock samples; thus if the soil anomalies are found to correspond with the primary anomalies in the parent rock, a soil-sampling survey is to be recommended.

Soil.—In stony soil it is usually easier to prepare sample holes with a pick and shovel. A geologic pick or a folding Army foxhole shovel has been found satisfactory for shallow holes. In clay soils, a soil auger is usually easier and faster than the pick-and-shovel technique. A suitable soil auger may be assembled by brazing or welding a large wood-auger bit to a section of light iron pipe, and attaching additional lengths of pipe as needed for greater depth; a T-shaped handle may then be fitted to the top section of pipe. It is found that the auger bit is more effective in cutting through soils if the leading screw point is cut out. If samples are to be taken at a predetermined depth, it may be easier to drive a crowbar into the soil for the required distance, remove the bar, and then extract the sample from the hole with an auger. Where deep holes are required, and where the terrane permits, the use of mobile power augers should be investigated.

The size fraction of soil used for analysis may make some difference in the significance of the data. In some problems it has been found that the metal content of the fine fraction was somewhat, but not greatly, higher than that of the coarse fraction. In other experiments, no significant variation with size was apparent. The standard procedure adopted for Geological Survey work has been to collect the fines (minus 80 mesh) for analysis and discard the coarse fraction. This avoids the need of grinding the sample before analysis and may cut down erratic data resulting from possible coarse fragments of oxidized ore minerals such as lead carbonate or malachite. An alternative procedure is to collect all sizes less than 2 mm in diameter and grind before analysis. This procedure may be preferable where the soil lacks an appreciable proportion of fines or where the ore metal is concentrated in the coarser sizes.

It is sometimes possible in dry climates to sieve samples as they are collected. Usually, however, fresh samples are so damp that the fines cannot be separated by sieving until the samples have had a chance to dry. Most samples may either be collected without sieving or, if desirable, sieved to minus 2 mm on the spot. If paper containers are used, such samples should be dry enough for sieving to the desired size in a day or two of storage in a dry room or in the sun without opening the containers.

Harold Bloom of the Geological Survey has conducted comparative experiments on sieves composed of brass, stainless steel, and silk, and has found that contamination of the sample by copper and zinc from brass screening under extreme conditions is less than 10 ppm. Thus, except for very precise work, the use of standard brass sieves is permissible. The advantage of stainless steel besides being noncontaminating is its strength and durability. It is considerably more expensive than other materials. Silk sieves are by far the least expensive of the three but are easily damaged and must be replaced frequently. A very economical noncontaminating sieve can be made by knocking the paper disc out of the cap of a half-pint ice-cream container, and using the remaining band to clamp a piece of silk bolting cloth. to the bottom section of the container.

For the standard field tests, the analyst needs about 5 grams of prepared material (sieved or ground). This leaves enough of the sample for possible repeat determination and for tests for more than one element if desired.

Paper containers are most commonly used for soils. For standard, mass-production work either 2-ounce paper cylinders sold by drug houses for pills, or manila envelopes with a metal clasp are usually satisfactory. For larger samples, cylindrical ice-cream containers have been widely used. The advantages of paper containers are low cost, usually less than a cent apiece, and convenience in handling. A serious disadvantage of paper containers is that they tend to become unglued when used for very wet samples. When this happens, it is necessary either to repair the container with scotch tape, or transfer the sample to a new container after drying. Paper containers constructed with heavy kraft paper and waterproof glue should be used if available.

Vegetation.—Samples of vegetation for chemical analysis should be taken far enough above the ground to be clear of contamination from rain spatter. Experience has shown that it is important to confine a geochemical plant survey to samples taken of the same organs of the same species to be sure of obtaining comparable data. The collector must, therefore, be able to recognize the species of tree that is to be used. Wood can be collected either from the main trunk with a carpenter's auger or from branches sawed or chopped off and stripped of leaves and bark. Where twigs are used, they may be removed either with a knife or a pruning device of some kind. Leaves and needles can most conveniently be removed from twigs by first allowing the sample to dry and then stripping off the brittle outer foliage. The same way of removing needles can be used in surveys where the metal content of the needles alone is required.

For most of the analytical procedures, a sample of at least 5 grams, dry weight, is required. The most commonly used containers are lightweight paper bags.

Water.—The collection of water samples presents a special problem not found with other kinds of material in that the content of traces of metals is relatively unstable. The most serious difficulty is the removal of ions from solution by adsorption to the walls of the vessel in which the water sample is stored. Metal may also be removed from solution by coprecipitation with the iron hydroxide precipitates that commonly form when water is stored for any length of time. It is reported that these effects can be minimized by acidifying the sample immediately after collection, in order to inhibit both exchange reactions and hydrolysis. If a soft-glass vessel is used, some of the metal contained in the glass may go into solution to contaminate the sample; this may be avoided by using containers made of either borosilicate glass or plastic. Polyethylene bottles with screw-cap tops are probably the most suitable, as they are not only free of contamination but also unbreakable.

Because of the serious difficulties in the storage of water samples, it is highly desirable to avoid these problems entirely by making the analyses on the spot using a portable analytical kit.

Stream sediments.—Where the heavy-mineral content of sediments is to be measured, it is usually desirable to collect the sample from the surface of bedrock beneath the stream channel. This may require either digging a pit or augering a hole, if the bedrock is buried beneath a heavy cover of alluvial material. Where the unstable component of the stream load is being mapped, suitable samples can be obtained from deposits of silt either in the stream bed or exposed under the sod or forest litter on the banks of the stream. Under some conditions samples from older alluvial terraces may be suitable.

The general problems of determining the optimum size fraction are the same for sediments as for soils, which have already been discussed. As with soils, about 5 grams of prepared material is adequate for most types of analytical work. For sediment samples, waterproof containers of some kind are mandatory, as nonwaterproof paper containers will disintegrate in contact with the moisture in normal sediment samples. Heavy paper envelopes made with waterproof glue are probably most satisfactory, as they permit drying of the sample without transfer and also provide a convenient surface for notes. Small aluminum containers have been widely used for sediment samples, as they are unbreakable, noncontaminating, and easily stored. A plastic (styrene) cylindrical container fitted with a friction-held polyethylene cap used for dispensing drugs appears to be equally suitable. Tinned steel has been found unsatisfactory because of rusting and danger of contamination from minor constituents in the tin plating. Cloth or polyethylene sacks would probably be satisfactory if rigid containers were not available.

Marking sample sites.—It is almost always desirable to mark the sample site in such a way that it can be found again if the area is revisited. It is rarely necessary to mark more than one out of three or four sites in a large systematic survey. Marking may be done by marked stakes, marked rags tied on bushes, blazes on trees, or pieces of paper left in the hole and anchored under a stone. Waterproof and weatherproof crayon of some kind saves the embarrassment of finding the mark illegible when the site is revisited.

Numbering samples.—In its geochemical prospecting work, the Geological Survey uses systems of simple accession number for each job so that samples are numbered consecutively with simple Arabic numerals in the order in which they are taken, regardless of the nature of the sample. Even so, skipped or duplicated numbers will turn up from time to time; when numbers are duplicated, both samples bearing the identical number become worthless and have to be resampled, often at considerable cost. This may be avoided by printing or writing a consecutive series of numbers on gummed tape and then tearing off the appropriate number from the coil of tape and pasting it on the container when the sample is collected. If envelopes or other flat containers are used, the number may be marked on the empty containers in advance. In addition to the number, every sample container should adequately identify the project. This may be done easily with a hand-set rubber stamp showing name of project, location, name of collector, and year.

CHOICE OF CONSTITUENTS TO BE DETERMINED

Choice of element.—The mapping of dispersion patterns formed by the major ore metals is the most straightforward approach. If zinc ore is sought, the distribution of traces of zinc would seem to give the most direct indication of the buried ore. A large part of the geochemical prospecting work to date has been based on this premise, and its sucess in finding ore justifies the assumption. Not uncommonly, however, the ore metals themselves fail for one reason or another to form a dispersion pattern that can be readily detected and mapped. In this event, consideration must be given to the distribution of associated noneconomic elements, or "pathfinders," as defined by Warren and Delavault (1953a). Pathfinders may be elements present in the ore in major amounts but not of commercial value, such as iron and sulfur (in pyrite), barium (in barite), or antimony (in tetrahedrite); common ore metals occurring in quantities too small to be commercially extractable, such as zinc (in most ores of copper and silver); or rare elements that are strongly enriched in certain ores, such as antimony, selenium, cadmium, and bismuth (table 3).

In a geochemical reconnaissance of a virgin area, where little or nothing is known about the kind of minerals in the area, the prospector must watch for all of the important ore metals. If every sample is analyzed for every one of these elements, the survey would almost certainly be an expensive undertaking and might turn out to be uneconomical. A less pretentious approach would be to analyze the reconnaissance samples only for a certain few selected elements that, taken together, occur in a wide variety of ore types. Zinc occurs as either a major or minor constituent of most base-metal ores and in some precious-metal deposits as well. Copper is associated with many ores of nickel, cobalt, molybdenum, and precious metals. Zinc and copper together, therefore, may be useful as indicators not only for zinc and copper deposits, but for many other types of ore. Other associations of metals that might be helpful in selecting key elements for reconnaissance are the tin-tungsten-niobium association in high-temperature veins and the rare elements in pegmatite deposits.

Most geochemical prospecting surveys, however, have been conducted in areas where it is possible to make an intelligent guess of the kinds of ore deposits that are likely to be found. In this event the plan of investigation can be guided by a knowledge of the characteristic dispersion patterns formed by the particular elements occurring in the type of ore that is expected. In the secondary dispersion cycle, immobile metals commonly form the most clear-cut patterns in residual soils, whereas the mobile metals tend to be dispersed more widely by movement in ground and surface waters and into the vegetation. Thus, where a mineral deposit is enriched in more than one metal, it may be most effective to test for the most mobile of the metals in the reconnaissance work and for the least mobile in the detailed soil survey. In prospecting for lead-zinc deposits, therefore, the reconnaissance may be based on zinc or total heavy metals and the detailed followup on lead. The cobalt ores of the Blackbird district of Idaho contain major amounts of both cobalt and arsenic. In weathering, arsenic is far less mobile than cobalt, with the effect that the arsenic patterns in residual soils delineate the mineralized areas far more sharply than the cobalt patterns.

In actual practice, the choice of the element to be determined is governed all too frequently by the availability of a suitable analytical test. It is earnestly hoped that continuing chemical research will eventually provide adequate tests for all the important elements that occur in ore deposits

Choice of extraction method.—Most geochemical prospecting work is based on the determination of either the total content of one or more elements in the sample or of an approximately proportional part of the total content—a part that will show the same general pattern as the total values.

An occasion may arise, however, where an element is bound up in the sample in more than one way, and where the mechanism of binding is related to the source of the element, whether normal rock or a mineral deposit. Such a situation is found in glacial soil, where part of the metal content is tied up in the lattice structure of primary rock-forming silicate minerals of no economic interest, and part originates from nearby ores by ground-water circulation and is loosely held by adsorptive forces. Here it would be highly desirable to differentiate the metal according to its two modes of origin. A weak extraction procedure adequate to remove the exchangeable metal, but not strong enough to break up the primary silicates, might give a better indication of the economically important dispersion pattern than a method involving total extraction of the metal.

Lovering, Sokoloff, and Morris (1948) describe a relationship of this kind in their study of primary halos in the Tintic district of Utah. They report that a weak extraction of metals from altered volcanic rocks overlying a concealed ore body gave a significant geochemical pattern that was not brought out at all by a total extraction method.

ANALYTICAL TECHNIQUES

In touching briefly upon the methods of chemical analysis used in geochemical prospecting, it is perhaps worth pointing out again that the purpose of a geochemical prospecting survey is to find ore deposits. The most economical method of chemical analysis that will provide the data by which ore deposits can be found is, almost by definition, the best. Expressed in a different way, the most suitable analytical procedure is one that embodies a satisfactory balance of reliability, economy, and promptness in reporting results.

Methods available.—A full discussion of the many procedures that have been developed for geochemical prospecting work is beyond the scope of this report; details may be obtained by consulting the references. The following list contains the principal references to colorimetric methods of analysis:

Metal	Material	References
Antimony	Soil and rocks	Ward and Lakin (1954)
Arsenic	Soil	Almond (1953b)
Cobalt	Soil and rocks	Lakin, Almond, and Ward (1952)
	Soil	Almond (1953a)
	Water	U. S. Geological Survey, p. 13.[9]
Copper	Soil and rocks	Lakin, Almond, and Ward (1952)
		U. S. Geological Survey, p. 16.[9]
	Plants	Warren and Delavault (1949)
		Stevens and Lakin (1949)
	Water	Lakin, Almond, and Ward (1952)
		Rosenqvist and Vogt (1943)
		Huff (1948)
Heavy metals	Soil and sediment	Lakin, Almond, and Ward (1952)
		Huff (1951)
	Water	Lakin, Almond, and Ward (1952)
		Warren, Delavault, and Irish (1951a)
		Riddell (1952a)
		Warren, Delavault, and Irish (1953)
		Huff (1948)
Lead	Soil and rocks	Lakin, Almond, and Ward (1952)
	Water	Huff (1948)
Manganese	Soil	U. S. Geological Survey, p. 32.[9]
Molybdenum	Soil and rocks	Lakin, Almond, and Ward (1952)
	Plants	Reichen and Ward (1951)
	Soil and rocks	Ward (1951a)
Nickel	Soil and rocks	Lakin, Almond, and Ward (1952)
	Plants	Do.
		Reichen (1951)
Niobium	Rocks	Ward and Marranzino (1955)
Silver	Soil and rocks	Lakin, Almond, and Ward (1952)
		Almond, Stevens, and Lakin (1953)
Tungsten	Soil	Lakin, Almond, and Ward (1952)
		Ward (1951b)
Uranium		Grimaldi, Ward and Fuyat (1954)
Vanadium	Rocks	U. S. Geological Survey, p. 39.[9]
Zinc	Soil	Lakin, Almond, and Ward (1952)
		U. S. Geological Survey, p. 16.[9]
		Lakin, Stevens, and Almond (1949)
	Plants	Lakin, Almond, and Ward (1952)
		Reichen and Lakin (1949)
	Water	Lakin, Almond, and Ward (1952)
		Warren, Delavault, and Irish (1951a)
		Huff (1948)

Spectographic methods of analysis were used widely for geochemical prospecting work during the prewar period. When determinations of more than two or three constituents are needed for each sample, semiquantitative spectrographic analysis is usually

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[9] U. S. Geological Survey, 1953, Additional field methods used in geochemical prospecting by the U. S. Geological Survey: U. S. Geol. Survey open-file rept.

more economical than the chemical methods. With the recent construction of a mobile spectrographic unit these methods may again have a wide application in geochemical prospecting, especially in reconnaissance work.

Methods employing paper chromatography have recently been developed for geochemical prospecting by chemists at the Chemical Research Laboratory of the National Physical Laboratory in Teddington, England. In preliminary experiments these methods show great promise, and it is possible that some of them will replace the rapid colorimetric methods now in common use.

Reliability.—Accuracy and precision of analytical data are not so important as the reliability with which the figures reflect the geochemical pattern. Most of the colorimetric procedures commonly used in geochemical prospecting were developed from the standard colorimetric methods of trace analysis by omitting or simplifying many of the steps needed for precise, quantitative work. As a result, the data contain errors that would not be tolerated in the average analytical laboratory. With the relatively weak extractants used in the rapid tests, rarely more than 80 percent of the total metal present in the sample will be measured. Furthermore, the reproducibility may be within a factor of only 1.5 or even 2.0 of the mean of several replicate determinations. Most geochemical anomalies, however, show a contrast of anomalous values against a background equal to many times the errors in the analytical tests. Thus, even with relatively inaccurate methods, as judged by usual chemical standards, the pattern should still appear.

One of the unavoidable consequences of the many shortcuts used in the procedures for the sake of speed is that seriously erratic analytical results will appear in a certain (usually small) proportion of the reported figures. The analyst has no way of knowing which of his figures may be questionable without running the entire lot in duplicate. The geologist familiar with his problem, however, is much better equipped to choose samples where the reported analysis does not seem to fit the geologic picture and to ask for confirmatory repeat analyses. This should be done by the geologist as a routine matter as soon as he receives an analytical report.

Cost.—With a properly equipped laboratory, one man can make 30 determinations per working day with most of the procedures developed by the Geological Survey. With a few of the procedures, the rate may be as high as 100 per man-day. The cost of materials and glassware is negligible, so that the bulk of the cost is in labor.

Promptness.—The promptness with which the field party needs analytical data varies with the nature of the exploration program. In the following drainage patterns, and particularly in analysis of stream water for metals, effective work almost requires that analyses be made on the spot. In experimental investigations preliminary to laying out a program of routine work, data are needed within a day or two of the time of collecting the sample and can best be provided by a mobile analytical unit at the base camp. Most of the colorimetric procedures can be set up under crude field conditions if necessary, and a few are adaptable for use at the sample site. In large-scale routine surveys where there is no call for immediate day-to-day decisions, however, samples can most efficiently be analyzed in some well-equipped central laboratory. Apart from the needs of the job for prompt data, the most efficient, reliable, and economical analytical work is done in an established laboratory.

PREPARATION OF MAPS AND DIAGRAMS

Clear and concise graphic plots of geochemical data make the task of interpretation much easier. Profile curves, in which the relative position of the sample sites is plotted on the horizontal axis and the geochemical data are plotted vertically, are useful for isolated sample traverses. Where the values vary over an extremely wide range, the use of a logarithmic vertical scale serves to bring the entire range into a scale that can be readily handled. Data for more than one component can be shown on the same diagram by using different symbols for the lines of the curves; if only two components are shown, the data for each may be plotted in opposite directions from the centerline, taken as zero. Geologic or other information may be added either as notes or as a separate diagram directly beneath the geochemical curve.

Geochemical plans are desirable where more than a single traverse line has been sampled. Sample locations may be marked by a dot, cross, or circle. The analytical data can then be lettered on the plan next to the symbol for the sample site. The scale of the map should be chosen so that the figures on the map are not crowded; a minimum distance of ¼ inch between symbols results in an attractive and legible map. Where more than one analytical figure must be shown for each sample, they can be plotted (1) on opposite sides of the symbol for sample location, (2) one over the other and separated by a horizontal line, or (3) in a consistent sequence separated by hyphens or semicolons. To save space and confusion on the map, it may be desirable to assign simple code numbers to represent ranges of values and to plot the code numbers in place of the figures reported by the analyst. Kennedy (1952) developed a particularly effective system of logarithmic code numbers to represent figures ranging from 50 to 50,000 ppm.

If possible, the geochemical data should be contoured by drawing "isograds," or lines of equal composition. When more than one set of figures is to be contoured on the same map, different styles of lines may be drawn for the different isograds. It is commonly found that the only useful contour that can be drawn on a geochemical plan is the threshold contour separating areas of anomalous values from areas of background values; additional contouring should be avoided as it congests the map and does not assist in the interpretation. However, lines connecting geochemical maximums should be drawn where possible to emphasize the axes of the anomalies.

In interpreting secondary dispersion patterns, consideration must be given to the slope of the surface and to the pattern formed by drainage divides and the drainage channels. The crests and spurs of ridges should be plotted on the geochemical map by a suitable symbol, and the pattern of streams, swales, springs, swamps, and alluvial flats by another set of symbols. The data of a geochemical survey of stream water or sediment can be generalized by shading in the basin upslope from any anomalous samples.

Simple geological information can be sketched directly on the geochemical map. If the geological patterns are complex, a transparent overlay is usually more suitable. Geochemical plans and diagrams should show (1) name and location of area, (2) scale and orientation, (3) explanation of symbols, (4) nature of samples, (5) analytical procedures, (6) units used in expressing analytical data, and (7) name of party chief, samplers, and analysts.

The methods of plotting data mentioned above are illustrated by the maps and diagrams published by Cannon (1952), Hawkes (1954), Huff (1952), and Kennedy (1952, 1956).[10]

INTERPRETATION

Accurate interpretation of geochemical survey data is the final step in effective geochemical prospecting. Effort expended in the planning and execution of the sampling and analytical work is wasted if the results are not understood. Skill in interpreting geochemical data must depend first upon general familiarity with the many factors that contribute to the formation of geochemical anomalies as discussed in this report and, secondly, on a specific

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[10] See also footnote 1 on p. 234.

knowledge of the balance of these factors in the area under study, such as may be gained from local orientation studies over known deposits.

No hard-and-fast rules can be given for the interpretation of geochemical data. The personal factor plays a major role. The following suggestions represents the writer's approach to the problem of interpretation. This approach is based upon finding the answer to three questions: (1) how do the anomalies form? (2) what is the theshold value of the anomalies? and (3) what can cause false anomalies?

More than one geochemical process can and usually does play a part in the formation of an anomaly. In residual soil, the pattern of residual metal owing to the weathering of ore in place is only one component of the pattern; metals may also be distributed in residual soils by solution and redeposition in ground water, by slumping, slope creep, frost action, and the activity of living organisms. Similarly, the pattern of metals in glacial till may combine the effects of glacial transportation, ground-water movement, ionic diffusion, and living organisms. An accurate interpretation of the significance of an anomaly, therefore, is not necessarily a simple matter. However, if the relative effect of each of the factors contributing to the formation of an anomaly is accurately appraised, an accurate over-all interpretation is much more likely.

Knowing the threshold value separating anomalous areas from background is a prerequisite to recognizing an anomaly. Inasmuch as the threshold is simply the upper limit of the normal variation in background values, an accurate estimate of the background range is of prime importance. Establishing the background should be one of the principal objectives of the preliminary orientation survey.

False anomalies are areas of high metal content that cannot be used as guides to ore. Under special circumstances, natural enrichments of metal can occur that have no genetic connection with ore or mineralizing processes. The normal enrichment of zinc in the ash of dwarf birches in concentrations as high as 1.0 percent is an example (Warren and others, 1952b). With an adequate understanding of normal enrichment processes, however, unusual concentrations of this kind can be recognized as lying within the normal background range for the particular material. The same cannot be said for the effects of human activity. False anomalies due to human contamination are an ever-present threat, even in remote areas. Contamination can be caused by (1) fragments of ore scattered over the surface near mines or prospects, (2) metal-rich mine water, causing false anomalies by ground- and surface-water circulation, (3) mineralized waste rock from mines used for general construction purposes or as an agricultural fertilizer, (4) trash containing metallic objects, (5) industrial waste water, (6) metal-rich dust from mine-tailings piles, (7) smelter fumes, smoke and fumes from industrial and urban areas, and exhaust fumes from motor vehicles, and (8) insecticide sprays. Every one of the above sources of contamination has at one time or another caused either trouble or concern in connection with the interpretation of geochemical data. Preliminary experiments in areas of suspected contamination should make it possible to recognize these effects when they are found in geochemical survey data.

GLOSSARY

Accumulator plant. A plant that takes up a particular element in quantities considerably in excess of that in "normal" plants (Robinson and Edgington, 1945).

Alluvium. Detrital material deposited by running water.

Background. The abundance of an element or any chemical property of a naturally occurring material in areas where the chemical pattern has not been affected by the presence of a mineral deposit.

Biogeochemical prospecting. Synonymous with geochemical plant survey.

Blind deposit. A deposit that does not extend to the surface of bedrock.

Botanical anomaly. A geochemical anomaly in which the chemical composition, ecological assemblage, or morphology of plants indicates the presence of a mineral deposit.

Contrast. A ratio expressing the geochemical relief, computed as the ratio either of maximum value to threshold, of maximum to background, or of threshold to background values.

Converter plant. A plant that takes up an insoluble element from the soil, builds it into its living structure, and at death returns it to the soil in soluble form.

Diffusion pattern. A dispersion pattern resulting from upward movement of ions in vadose water.

Dispersion pattern. A pattern of distribution of chemical elements resulting from the movement of natural materials.

Ecology. The study of relationships between organisms and their environment.

Extractable metal. A metal that can be extracted from a sample by any given chemical treatment.

Fan. A dispersion pattern that spreads predominantly to one side of the source of material.

Genetic halo. A geochemical anomaly resulting from primary dispersion.

Geochemical anomaly. Area where the chemical properties of a naturally occurring material indicate the presence of a mineral deposit in the vicinity.

Geochemical prospecting. Mineral exploration based on systematic measurement of the chemical properties of a naturally occurring material.

Geochemical province. An apparent local variation in the original composition of the earth's crust.

Geochemical survey. A survey involving the chemical analysis of systematically collected samples of rock, soil, plants, or water; this expression may be further modified by indicating specifically the material sampled, as, for example, "geochemical soil survey."

Geochemistry. The study of the distribution of elements in the earth.

Halo. A nearly equidimensional dispersion pattern, spreading symmetrically upward or outward from the source of material.

Heavy metals. Metals that react readily with dithizone, principally zinc, copper, cobalt, and lead, but under special conditions including one or more of the following metals: bismuth, cadmium, gold, indium, iron, manganese, mercury, nickel, palladium, platinum, silver, thallium, and tin.

Hydrogeochemical prospecting. Synonymous with geochemical water survey.

Indicator plant. A plant that indicates by its presence the occurrence of an element in the soil upon which it grows (Beath, Gilbert, and Eppson, 1939).

Leakage halo. A dispersion pattern formed in the rock overlying a mineral deposit by the movement of ore-forming fluids through a well-defined system of channels.

Mobility. The tendency of an element to move in a given geochemical environment.

Pathfinder. A mineral or element found in close association with the element being sought, which can be more readily found or which has more obviously anomalous features than the element which is the main object of search (Warren and Delavault, 1953a).

Pedogeochemical prospecting. Synonymous with geochemical soil survey.

Plant symptom. An abnormal growth habit of a plant indicative of a peculiarity in the chemical composition of the supporting soil.

Primary dispersion. Geochemical dispersion of elements by processes originating within the earth; opposite of secondary dispersion.

Regolith. Loose surface material overlying solid rock.

Secondary dispersion. Geochemical dispersion of elements by processes originating at the surface of the earth; opposite of primary dispersion.

Sediment. Solid material deposited by running or standing water.

Soil. In agriculture: loose surface material capable of supporting plant growth, and having properties resulting from the integrated effect of climate and living matter. In geology: any loose surface material overlying solid rock; synonymous with regolith.

Soil formation. The process whereby fragmental material resulting from rock weathering is transformed into a medium that can support plant growth.

Soil horizon. A layer of soil, approximately parallel to the surface, which differs from adjacent layers in chemical and physical properties; the principal horizons from the surface downward are (1) the topsoil, *A* horizon, or leached horizon; (2) the subsoil, *B* horizon, or horizon of accumulation; and (3) the parent material, *C* horizon, from which the upper horizons were formed.

Soil profile. The vertical sequence of soil horizons.

Suboutcrop. Area of intersection of a geologic feature with the surface of bedrock beneath the regolith.

Superimposed halo. A dispersion pattern formed in the regolith by the movement of material in subsurface waters.

Threshold. In geochemical prospecting: the limiting anomalous value below which variations represent only normal background effects and above which they have significance in terms of possible mineral deposits. In analytical chemistry: the limiting sensitivity of an analytical method.

Train. A linear dispersion pattern resulting from movement along well-defined drainage channels.

Wall-rock halo. A dispersion pattern formed in the rock adjoining mineral deposits where the chemical composition has been modified by the ore-forming fluids.

UNITS OF MEASUREMENT

The units of measurement commonly found in the literature of geochemical prospecting are defined in tables 11, 12, and 13. The common unit of weight is the microgram, equal to a millionth of a gram and represented by the Greek letter gamma (γ). For solid material the common unit of concentration is the part per million (ppm), equal to 0.0001 percent. In expressing data on the composition of plants, the basis of measurement, whether ash or dry weight of the plant, should be specified. For aqueous solutions, concentrations may be expressed as parts per million (micrograms per milliliter) or micrograms per liter. Parts per billion should be avoided because of the difference in the American and British usage of the term billion.

TABLE 11.—*Units of weight*

Unit	Symbol	Metric equivalent (grams)
Metric ton	t	1,000,000
Kilogram	kg	1,000
Gram	g	1
Milligram	mg	.001
Microgram, gamma	γ	.000001
Short ton	----------	907.180
Avoirdupois pound	lb	453.6
Avoirdupois ounce	oz	28.35
Troy ounce	℥	31.10
Assay ton	----------	29.166

TABLE 12.—*Units of concentration*

Unit	Symbol	Proportionality
Grams per gram	g/g	1
Percent	%	.01
Milligrams per kilogram	mg/kg	.000001
Parts per million	ppm	.000001
Grams per metric ton	g/t	.000001
Micrograms per liter	γ/liter	.000000001
Milliequivalents per 100 grams	meq/100g	.00001 × eq [1]
Troy ounces per short ton	oz/t	.000034

[1] An equivalent (eq.) is the weight in grams which in its reaction corresponds to a gram-atom of hydrogen. For our purposes, it is taken as being numerically equal to the atomic or molecular weight divided by the valence. One thousand milliequivalents (meq.) is equal to one equivalent.

TABLE 13.—*Conversion table, units of concentration* [1]

B A	g/g	Percent	ppm	γ/liter	meq/100 g	oz/t
g/g	1	100	10^6	10^9	10^5/eq	2.9×10^4
Percent	.01	1	10^4	10^7	10^3/eq	2.9×10^2
ppm	10^{-6}	10^{-4}	1	10^3	10^{-1} eq	2.9×10^{-2}
γ/liter	10^{-9}	10^{-7}	10^{-3}	1	10^{-4}/eq	2.9×10^{-5}
meq/100g	eq × 10^{-5}	eq × 10^{-3}	eq × 10	eq × 10^4	1	eq × 0.29
oz/t	3.4×10^{-5}	3.4×10^{-3}	34	3.4×10^4	3.4/eq	1

[1] To express concentration in terms of "*B*," multiply concentration expressed as "*A*" by factor shown.

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