CONGRESO GEOLOGICO INTERNACIONAL

XXª Sesión — Ciudad de México, 1956

SYMPOSIUM DE EXPLORACION GEOQUIMICA

(PRIMER TOMO)

MEXICO, D. F.
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INTRODUCTION TO SYMPOSIUM ON GEOCHEMICAL EXPLORATION
XX INTERNATIONAL GEOLOGICAL CONGRESS

T. S. LOVERING *

The basic philosophy of geochemical exploration is that mineralo-genetic provinces, potential mining districts or oil fields, and individual deposits, even through hidden, may show diagnostic variations in the chemical composition of accessible materials that can be detected by sensitive analytical methods. Its broad field touches biochemistry, soil science, geology, and geochemistry, and depends primarily on the use of methods of trace analysis to bring to light the invisible but significant differences in composition that betray the presence of target areas.

Although geochemical exploration is as ancient as the art of panning gold, the modern techniques of trace analysis were first used about a quarter of a century ago for detecting low but anomalous concentrations of metals only a little above the clarke or general background of the metal. Russian and Scandinavian geologists began to use such methods successfully in the early 1930s', and a few years later some attention was given to geochemical exploration for petroleum by American companies. Outside the USSR, however, little curiosity was shown about this new tool for mineral exploration until after World War II, when interest in it spread rapidly through the United States, Canada, and Great Britain. It is fair to say that since 1950 interest in geochemical prospecting has become world wide, as is evident from the sources of the contributions to this volumen! Prior to the Symposium on Geochemical Exploration here in Mexico City at the Twentieth International Geological Congress, the number of publications in this new field of endeavor was far from commensurate with the current activity. In this symposium for the first time we find an adequate coverage of the diverse problems with which geochemical exploration grapples, and a fair indication of the possibilities of utilizing geochemical techniques in finding mineral deposits.

The wide range of subjects covered in the Symposium on Geochemical Ex-

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* *Coordinator, Symposium on Geochemical Exploration.*

ploration is instructive. The papers range from the broadly theoretical to the specific and practical, and in each group we find an amazing variety of stimulating contributions: reports showing how the variation in the ratio of the isotopes of oxygen in dolomite may lead to the discovery of hidden districts, or how the variations in the tin content of biotite may allow discrimination between granites that have tin deposits associated with them and granites that do not; papers describing the use of botanical methods for finding uranium in the arid Colorado Plateau of the western United States, and biogeochemical methods of prospecting in the peat swamps of Finland; the use of bromine-to-chlorine ratios in prospecting for potash, and the use of ethane-methane ratios in prospecting for petroleum, studies of geochemical prospecting techniques suitable to the tropics, and techniques applicable to permafrost areas of northern Canada; descriptions of analytical methods suitable for geochemical exploration, and descriptions of current governmental programs for carrying out research and discovery work in this new field. Such variety cannot fail to have something of interest for all exploration-minded geologists!

Readers will be impressed, I am sure, with the high quality of the many papers included in the symposium, and with the generosity displayed by both commercial and governmental organizations as well as by individual consultants in making available information of great value not only to the professions but to themselves. It is hoped that the splendid example set by all these participants in sharing their information will go far toward discouraging the tendency in certain fields of mineral exploration to capitalize on common knowledge through the media of patents applied to general principles. Only through the free exchange of information can we hope for the healthy growth of any branch of science; this is especially true in the early stages of the development of geochemical exploration, and realization of this truth and appreciation of the cooperative progress so clearly evident probably accounted for the satisfaction and pleasure in the symposium expresed by audience and contributors alike. My congratulations to all the participants!

Denver, Colorado
August 1957

SÉANCE MATUTINALE DU 6 SEPTEMBRE 1956

PRESIDENCE DE M. J. ORCEL

Mes chers Collègues,

Je tiens à dire d'abord combien j'ai été sensible à l'honneur que m'a fait le Comité exécutif d'organisation du Congrès en m'appelant à présider une partie de cette séance.

Peut-être a-t-il voulu souligner l'apport du Laboratoire de Minéralogie du Muséum de Paris, et en particulier celui du regretté professeur A. Lacroix, à la détermination de la composition chimique des minéraux et des roches ainsi qu'à la connaissance de leurs associations caractéristiques et de leur genèse dans le temps et dans l'espace.

Au nom de ce laboratoire j'adrese donc au Comité du Congrès de bien vifs remerciements.

Permettez-moi en introduction à cette séance, de vous présenter quelques très brèves réflexions sur l'orientation des recherches géochimiques.

Le Congrès actuel, que l'on peut considérer comme le cinquantième anniversaire du Congrès de Mexico de 1906, marque en même temps une étape dans le développement de la géochimie.

En effet, en 1906, on ne prononçait que rarement le mot de géochimie, cependant introduit dans la littérature scientifique en 1838 para le chimiste suisse Schönbein.

Toutefois, sans ce mot, de nombreux résultats avaient été rassemblés, qui préparaient l'édification de la science nouvelle, sur la base des recherches des minéralogistes et des chimistes de nombreux pays.

Dans cet immense labeur dont le développement a commencé au cours de la première moitié du 19ème siècle, on peut distinguer trois directions essentielles:

1º—Une première orientation suivie et qui conserve toujours sa valeur est celle de l'étude systématique des *paragenèses minérales* qui débute avec le remarquable travail de A. Breithaupt (1848). définir les divers types de successions minérales qui constituent certaines lignées génétiques, et à établir des schémas d'ensemble très important comme ceux de Brögger (1890) et Fersman (1932) pour les pegmatites, de Sandberger (1885) sur les filons hydrothermaux, de Vant'Hoff (1903) pour des dépôts de sels, etc...

2º—La seconde direction que l'on peut envisager dans l'histoire de la géochimie est celle qui est orientée vers des buts pratiques, liés à la prospection des gîtes métallifères. C'est précisément cet aspect qui nous préoccupe dans la session de ce matin. Des lois nombreuses ont été mises en évidence concernant la répartition des minéraux et en même temps celles des éléments chimiques utiles. Cette orientation de recherches est représentée par la *métallogénie* dont bien des aspects constituent des transitions vers la géochimie dans sa physionomie actuelle. Ses pionniers furent principalement L. de Launay (1913), Lindgren et Emmons (1922-1923), Niggli (1925) et aussi Fersman (1930).

3º—Enfin, la troisième direction est celle qui se donne pour but l'approfondissement de problèmes théoriques que pose l'origine de la répartition des éléments chimiques et de leurs combinaisons dans les diverses enveloppes du globe terrestre. Les artisans les plus brillant de ces premières acquisitions de la géochimie théorique furent: F. W. Clarke, W. Vernadsky (1910-1933) et l'école de Goldschmidt (1924-1936) et de Fersman.

Il était obligatoire qu'au cours de son développement, la géochimie bénéficie des apports d'une autre science, la *chimiephysique*, dont le développment a débuté à peu près à la même époque que celui de la géochimie. Toute une série de notions et de concepts généraux sont alors élaborés en fonction des progrès de nos connaissances sur la structure de l'atome et de ses enveloppes électroniques. Tels sont les notions de rayons ioniques, de potentiels ioniques, de potentiel d'ionisation, de polarisation des ions et des atomes, qui affinent notre connaissance des propriétés du milieu cristallin, et qui permettent de comprendre de mieux en mieux les transformations que celui-ci subit au cours de l'évolution de l'écorce terrestre.

A un niveau supérieur d'abstraction et d'extension, sont définis par plusieurs auteurs les concepts de cycles géochimiques, d'enveloppes thermodynamiques, et une série de généralisations basées sur la classification périodique des éléments. Et actuellement, le développement considérable de nos connaissances sur la structure du noyau des atomes et sur la radioactivité a enrichi la géochimie d'un domaine de recherches nouveau, lié à la notion d'isotopie, domaine en plein essor, et dont on mesure déjà nettement l'importance pour la géologie à la fois du point de vue théorique et du point de vue pratique: car l'étude des répartitions des isotopes peut nous éclairer sur le processus de dispersion et de concentration des éléments chimiques.

On voit donc comment s'est imposée à la pensée du géochimiste la notion d'atome. Il lui a donné peu à peu la priorité sur la notion d'espèce minérale, et la géochimie a été définie comme la science des lois de migration, de dispersion et d'accumulation des éléments chimiques dans les diverses couches de l'écore terrestre, et dans l'atmosphère.

Cependant la notion d'espèce minérale conserve toute son importance, car les minéraux, résultats de réactions entre les éléments chimiques sont autant de manifestations sensibles de l'union passagère de ceux-ci au cours de l'évolution du globe. Le géochimiste peut donc se dispenser d'en connaître parfaitement toutes les propriétés et tous les modes de associations. Car c'est par le cristal que le géochimiste atteint l'atome dans ses migrations.

Ainsi ressort toute l'importance pour le géochimiste des recherches de *cristallochimie.*

Car le processus naturel de la repartition et de l'association des éléments chimiques, c'est-à-dire de la formation des minéraux et des roches, consiste fondamentalement dans le fait que des ions mobiles, contenus dans divers milieux générateurs (solutions aqueuses, fluides volatils, magmas, milieux solides évoluant dans des conditions particulières encore mal définies), se transforment en systèmes moins mobiles, plus stables, qui sont les cristaux, dont la structure géomètrique est le reflet d'un certain équilibre de nature électrostatique entre les atomes ou les ions.

Ainsi, du point de vue énergétique, le passage à l'état cristallin représente un processus de transformation en un état plus stable et plus pauvre en énergie.

Donc, plus un ion dégagera d'énergie sous une forme ou sous une autre, en contribuant à la formation d'un édifice cristallin, plus il sera difficile de le ramener de nouveau à l'état dispersé, plus il sera apte à s'accumuler en masses importantes dans l'écorce terrestre pour former un gisement exploitable de cet élément.

C'est précisément ce problème qui nous intéresse en métallogénie et dans la prospection géochimique. La nature du réseau cristallin formé (structure et motif) détermine un certain nombre de propriétés physiques et chimiques spécifiques du minéral.

Ces propriétés varient suivant le type du réseau, les distances réticulaires, les relations entre les forces de liaison que l'on peut définir dans le cristal. Ainsi est introduite la notion de *champ cristallin,* par laquelle on peut pénétrer plus profondément dans l'essence même du cristal, dans sa structure, dans l'analyses des mouvements de la matière qui le constituent.

Tous ces caractères importants du point de vue géochimique sont mathématiquement liés; leurs relations sont définies par l'énergie réticulaire, et la répartition de l'énergie entre les divers atomes et ions à l'intérieur du cristal.

Cependant ces calculs effectués directement à partir de la théorie sont inextricables.

De sorte que pour avancer vers la connaissance intime du champ cristallin, il faut recourir à l'expérience. C'est pourquoi on étudie les lois de l'agitation thermique des atomes, car elles découlent du champ de force inconnu qu'il s'agit d'étudier.[1]

Je ne puis évidemment insister ici sur ces recherches qui mettent en oeuvre la diffusion des rayons X, l'effet Raman, le rayonnement infrarouge, les ondes électromagnétiques centimètriques qui agissent par exemple sur les spins électroniques, les spins nucléaires ou les moments quadrupolaires nucléaires. Toutes ces recherches ne peuvent laisser le géochimiste indifférent, et l'une de ses tâches sera de les adapter aux exigences spécifiques de la science.

Les travaux anciens de Fersman[2] sur la notion des coefficients énergétiques (Ek et Vek) ont constitué une étape importante dans cette direction.

Je rappellerai que ces coefficients déterminent la quantité d'énergie émise par un ion lorsqu'il passe de l'état dispersé à celui d'ion, ou d'atome inséré dans un réseau cristallin, Vek étant le coefficient Ek rapporté à l'unité de valence.

Ces coefficients définissent donc le degré de solidité des liaisons interatomiques, et la notion qu'ils représentent a été introduite à partir d'une formule générale donnée par Kapustinsky en 1933 pour exprimer l'énergie réticulaire U (en k/calories) sur la base de la théorie de Born. Cette formule fait intervenir la notion de potentiel ionique ou rapport de la valence d'un ion à son rayon.

Certes, des critiques justifiées ont été faites (en partie récemment par Lebedeff[3]) au sujet de ces notions qui consistent à considérer un peu trop exclusivement les combinaisons hétéroatomiques du point de vue de la liaison électrostatique ionique, étant donné qu'il faut tenir compte aussi du rôle joué par les autres types de liaison (homopolaire ou même de Van der Vaals) dans un grand nombre d'édifices cristallins.

Néanmoins, il semble bien que la géochimie tirerait le plus grand profit de recherches nouvelles dans le sens indiqué par Fersman, mais en utilisant les plus récentes acquisitions de la cristallochimie.

Je ferai enfin une dernière remarque: Dans son sens le plus général, la géochimie englobe aussi l'étude des lois de distribution des éléments chimiques, non seulement dans l'écorce terrestre, mais aussi dans l'hydrosphère, dans l'atmosphère et dans la biosphère, et, étant donné, l'importance des interactions entre les phènomènes de la vie et la matière terrestre, une nouvelle science s'est constituée, la biogéochimie, et nous allons entendre au cours des séances de travail de notre section plusieurs communications se rapportant à ce domaine de recherches.

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[1] Cf. H. CURIEN. 1954. Aspects cristallographiques de la Physique, *Revue générale des Sciences*, LXI:88-93.

[2] A. E. FERSMAN. 1937. *Géochimie*. Leningrad, t. III (en russe).

[3] V. J. LEBEDEFF. 1953. Quelques observations sur la Géochimie en tant que Science. *Izvestia Acad Nauk U.R.S.S.*, *Serie Geologie*, nº 3 (en russe).

D'autre part, l'étude approfondie des météorites, certaines données de l'astrophysique et de la cosmogonie sur la formation des planètes la formation d'un nouveau domaine scientifique ayant ses buts propres mais étroitement apparentés à la géochimie. C'est le domaine de la *cosmochimie.*

L'essor de la géochimie et des sciences soeurs, l'intérêt que lui porte un nombre toujours plus grand de chercheurs venant des divers horizons de la science (physiciens, chimistes, géologues etc...) se sont tellement accrus en ces dernières années quuun périodique spécial a été créé, *Geochimica et Cosmochimica Acta,* que vous connaissez bien, qu'un autre périodique vient d'être créé en URSS sous l'impulsion de M. Vinogradov, que la *Chronique des Mines coloniales* signale et analyse dans une rubrique spésiale les travaux de géochimie et que deux société géochimiques se sont formées, l'une en France, l'autre en Amérique, qui sont déjà bien vivantes. Mais je ne veux pas retenir plus longtemps votre attention, dont je vous remercie, car notre ordre du jour est très chargé.

Je vous prie de m'excuser de l'avoir alourdi et j'adresse un salut cordial à tous les membres du Congrès qui participent à cette séance.

I – GEOCHEMICAL PRINCIPLES APPLICABLE TO GEOCHEMICAL PROSPECTING

VARIATIONS IN THE ISOTOPIC COMPOSITION OF OXYGEN IN THE LEADVILLE LIMESTONE (MISSISSIPPIAN) OF COLORADO AS A GUIDE TO THE LOCATION AND ORIGIN OF ITS MINERAL DEPOSITS

A. E. J. Engel, * R. N. Clayton * *
and S. Epstein * *

ABSTRACT

Oxygen isotope studies, integrated with geologic investigations of the Leadville limestone and associated ores, help clarify the origin and whereabouts of these and possibly other mineral deposits. In the Leadville widespread uniform beds of limestone, dolomite, and chert which exhibit no hydrothermal alteration contain oxygen isotopically approximating that in other "unaltered" carbonate sediments of pre-Mesozoic age. Moreover, isotopic fractionation measured between calcite and quartz also suggests the beds crystallized at near-surface temperatures.

In contrast, quartz and carbonates in the great dolomite halos that are spatially and temporally related to ore yield a range of oxygen isotope values, all lower in 018, indicative of much higher temperatures. Differences in oxygen isotopes in quartz, dolomite, and rare calcite are fairly systematic with respect to ore and obvious conduits. Highest temperatures are indicated at ore and feeders.

Successively lower temperatures of formation of the dolomite halo are indicated toward its perimeter 2 to 15 miles away. In these dolomite halos variations in structure, texture, and concentration of elements and minerals are seemingly unsystematic with respect to ore. Hence the variations in oxygen isotopes may represent a useful guide to ore.

INTRODUCTION

In the Leadville limestone of central Colorado, the identity and relations of unaltered sedimentary beds to masses of hydrothermal dolomite may be determined in numerous widely distributed exposures. Most of the unaltered beds are microsystalline limestone, partly very pure, partly chert-bearing. Bedded sandy dolomite and thin beds of (diagenic?) dolomite occur, however, in the lower one-third of the formation. Most of the beds (in the Leadville) are monotonus in composition and texture, and laterally persistent throughout an area

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of some 5000 square miles in central Colorado. Some of the best exposures of unaltered Leadville limestone are in the White River Plateau and Sawatch Range. A geologic map of this region constitutes Figure 1.

At intervals in this region, particularly on the slopes of the Sawatch Range, the Leadville limestone is replaced by metal sulfides, especially pyrite, sphalerite, galena, and chalcopyrite. The sulfide mineralization at Leadville and Gilman, Colorado is especially extensive and commercially important.

Around the large deposits of metal sulfides ,most or all of the original limestone is replaced by dolomite. The close and consistent spatial and paragenic relations of this dolomite to ore, along with other geologic criteria, indicate that the dolomite is of hydrothermal origin and has formed as a phase of the mineralizing epoch.

The seeming clarity of the relations of initially uniform carbonate beds to hydrothermal dolomite and ore, suggested a study of the geochemical properties of these several rock types. This paper discusses one phase of the geochemical study, namely the isotopic composition of the oxygen and carbon in unaltered and hydrothermal segments of the Leadville formation. Analyses have been made of the 0^{18} and 0^{16} content of the oxygen in the unaltered sedimentary limestones, cherts, and the bedded (diagenic) dolomites, and in stratigraphically equivalent zones of hydrothermal dolomite and associated silica. Carbon isotope analyses have been made of most carbonates that were analyzed for exygen isotopes.

PHYSICAL STRATIGRAPHY OF THE LEADVILLE LIMESTONE

The beds within the unaltered Leadville limestone can be grouped into three major units, as diagrammed in the columnar section on the left hand side of Figure 2. The basal unit, named the Gilman sandstone member (Lovering and Tweto, 1944; see Tweto, 1949, p. 177-184), is sandstone and sandy and cherty dolomite, and commonly includes a median breccia of these rocks. The thickness of Gilman sandstone member varies from 1 to 40 feet. The member is widespread throughout central and northwestern Colorado at the base of the Leadville limestone.

The middle member of the Leadville formation is cherty, gray limestone, medium-grained to very fine-grained. Commonly several beds of fine-grained dolomite occur at and near the base of this unit. Atlhough all of the dolomite beds are laterally extensive, one that ranges from 2 to 8 feet in thickness lies at the base of the cherty limestone member throughout central and northern Colorado. The dolomite in this basal bed is fine to very fine-grained, and buff to gray in color. It maintains its fine-grained, dense texture even in the areas where all of the calcitic beds are replaced by hydrothermal dolomite. Locally very thin black chert layers occur at or near the top of this bed. In the mines at Gilman, Colorado, this dolomite has a dense brown almost waxy appearance, and it forms what is referred to locally as the "waxy bed". For convenience this name will be employed to designate this bed, which we have sampled and analyzed at widely separated localities within and outside the halos of hydrothermal dolomite (Fig. 2 and Table 1).

The thicker, middle member of the Leadville formation ranges from 15 to 70 feet in thickness, averaging about 40 feet, an is dominantly cherty limestone. Dark gray to black chert is more abundant near the base and top of the member, but rarely exceeds 4 per cent of the total rock. The limestone itself contains from 2.5 to 3.2 weight per cent silica in disseminated microcrystalline form. Total non carbonate constituents other than silica —chiefly Al, Fe and Mg— are not abundant however, rarely totaling more than 0.5 weight per cent. This cherty unit is readly distinguished even in places where the formation has been completely converted to hydrothermal dolomite.

The uppermost and thickest of the three major subunits in the unaltered Leadville is a remarkably pure, gray limestone. It often forms massive, bluish-colored cliffs that have caused the name blue limestone to be applied rather loosely to the entire Leadville formation and the underlying Dyer dolomite. This limestone member is commonly from 60 to 150 feet thick, averaging about 80 feet in the White River Plateau. Major deviations from this thickness are induced mainly by post-Leadville erosion and supergene solution. Fragments of fossils and oolites are common in parts of the upper limestone. Non-calcite constituents are rare, and most beds conmmonly contain about 99.0 weight per cent calcite. Grain size varies from fine to very fine. In most areas of hydrothermal dolomitization, the upper member of the Leadville is easily recognized by the abundance of the distinctive, inequigranular, striped, vuggy dolomite (zebra rock) that has formed in it as well as by its position between the cherty limestone member and the overlying shale of Pennsylvanian age (Fig. 2).

The lateral persistence and uniformity of the three members of the Leadville, and of many subunits, are of particular value in this study. Beds of dolomite, chert and limestone can be followed to, through and beyond numerous deposits of metal sulfides and their sheath of hydrothermal dolomite. Each of many beds, where unaltered, maintain distinctive physical and chemical features, including a uniform and consistent oxygen isotope composition. These properties permit the unaltered beds to be used as bases of reference against which changes in oxygen (and carbon) composition induced by hydrothermal processes may be compared and contrasted.

HYDROTHERMAL DOLOMITE

The size and pervasiveness of the hydrothermal dolomite bodies seems to reflect at least crudely the scope and intensity of the associated sulfide mineralization. For example at mining districts such as Fulford, Aspen, Alma, Tincup and Monarch, the known deposits of metal sulfides are small to moderate in size. This also is true of the associated halos of hydrothermal dolomite that have replaced the original limestone.

The largest known deposits of sulfides and the largest halo of hydrothermal dolomite occur in the Leadville-Gilman region, on the east slope of the Sawatch range (Fig. 1). There the Leadville formation is dolomitized throughout its full thickness over an area of 200 square a series of major conduits, marked in part at least, by the great ore bodies at Leadvide and Gilman.

The many mine openings and drill cores in this region offer excellent sources of hydrothermal dolomite from various parts of the formation and at various distances from known ore. The simplicity of the geology at Gilman compared to that of the Leadville district, Colorado, suggested Gilman as a promising place to begin geochemical studies around ore. At Gilman, drill holes and mine and surface exposures permit sampling of the dolomite from known ore to the edge of the hydrothermal dolomite, near Minturn, some 2 miles to the northwest. Most of our isotope analyses of carbon and oxygen in hydrothermal dolomites are from the Gilman-Minturn area (Table 1).

Near Gilman, 3 of the 4 mayor stratigraphic units in the Leadville exhibit a characteristic type of dolomitization. The Gilman sandstone member appears little changed. The sand grains have not recrystallized, and the associated dolomite remains medium to fine-grained and dense. As noted earlier, the dolomite at the base of the cherty limestone also is unchanged; it is fine-granied, dense, and almost waxy in appearance, hence its name "waxy bed". Most of the cherty, fine-grained limestone in this member above the waxy bed is, however, converted into medium to fine-grained dark gray dolomite (Figure 2). Locally this dark, dense dolomite is striped by veinlets of more coarsely crystalline lighter gray to white dolomite, forming the rock described below as zebra rock. Some of the chert remains microcrystalline and dark gray, but at and near sulfides the chert nodules are peripherally bleached and recrystallized.

The upper, pure limestone member of the Leadville is largly replaced by the very striking inequigranular striped dolomite referred to as zebra rock, very similar to the striped dolomite formed locally in the underlying cherty member. This rock is streaked by generally subparallel veinlets of lighter gray to white more coarsely crystalline dolomite in a matrix of darker, finer-grained dolomite. The streaks tend to parallel bedding, although in many places they diverge 10 to 30 or more degress from it. Numerous vugs up to an inch or more across occur in the lighter colored, more coarsely crystalline dolomite. Crystals of white dolomite and quartz commonly proyect inward in these vugs. Pyrite occurs in them much less frequently.

The gray to almost black color of the fine-grained, denser dolomite in the zebra rock seems due almost entirely to included carbonaceous material. There are no obvious differences in the concentrations of other elements although there are striking differences in the isotopic composition of oxygen in the two rocks.

The dark dolomite phase of the zebra rock obviously formed before the coarse, lighter veins. The crystals of white dolomite, quartz, and pyrite in the vugs seem to have formed last. The impression gained is that during and after its formation, the darker, finer-grained dolomite was incipiently fractured along or subparallel to bedding. These discontinuities then served as loci for recrystaliiaztion to coarser dolomite with the expulsion of carbonaceus matter. Some solution of dolomite occurred after partial recrystallization, and this was followed by the growth of white dolomite, quartz and pyrite in the solution openings.

Aside from the zebra rock and dark dense dolomites, a third type dolomite, designated as "pink breccia", is especially noteworthy. The pink breccia occurs as a narrow zone or as zones up to 8 feet thick at or near the base of the upper member of the Leadville limestone (Fig. 2). It consists of rounded fragments of dense, medium to fine-grained, light-gray to pale-pink dolomite in which both angular and rounded fragments of the same material are vaguely to clearly discernable. The pink breccia follows bedding in most places but locally it cuts across beds; it seems to be confined largely to the hydrothermal dolomite of the Gilman area.

At various sites in all the hydrothermal dolomite bodies, but most commonly near ore, incipient but pervasive solution of the rock has occurred. Bonds between grains of dolomite are weakened and a highly friable dolomite, grading into dolomite sand, have been produced. The exact paragenic relations of the dark dense dolomite, zebra rock and hydrothermally sanded dolomite to ore have been the subject of extensive investigation by many geologists. The distribution and concentration of Cu, Pb and Zn in the dolomite (Engel and Engel, 1956) suggests that most hydrothermal dolomitization was accomplished by solutions essentially barren of metals, in an early stage of the oreforming epoch. Hydrothermal sanding ocurred at a later stage, after dolomitization, and at the onset, and possibly to a limited degree, during and after sulfide mineralization.

The relations of dolomitization and ore formation at Gilman, Colorado, are summarized by Lovering and Tweto as follows:

> "The —Leadville— was dolomitized during the first stages of mineralization. During the period of zebra rock development, alternating stages of leaching and precipitation recrystallized the dolomitized rock into the striped zebra rock over wide areas. Dolomite and zebra rock were later brecciated and recrystallized to form the pink breccia zone at about 95 feet above the Gilman sandstone, and in the last stages preceding ore deposition, dolomite, zebra rock and Pink Breccia were attacked by solvents and extensively sanded, and a network of open channels and caves was formed. Sulfides then replaced solid or brecciated dolomite, zebra rock, pink breccia, and sanded dolomites ....". (Lovering and Tweto, 1944).

ISOTOPE ANALYSES

The oxygen and carbon isotope analyses were done with a mass spectrometer (Mc Kinney *et al*, VTEJQ using carbon dioxide gas. The carbon and oxygen from the carbonates were analyzed by using carbon dioxide produced by reacting the carbonate with 100 percent phosphoric acid. The oxygen of the silica was extracted by heating the silica with graphite at approximately 1,800-2,000° C which produces carbon monoxide. The carbon monoxide, when cycled over a nickel catalyst at approximately 400° C and then through a liquid nitrogen coled trap, is converted quantitatively to carbon dioxide. The reproducibility of results is about ± 0.1 per mil. The procedures are discussed in detail elsewhere (Clayton, 1955; Clayton and Epstein, 1957).

Results of the analyses of isotopes of oxygen and carbon in the unaltered Leadville and in hydrothermally altered derivatives are listed in Table 1.

The results of oxygen and carbon isotope analyses are expressed as the deviation per mil or the O^{18}/O^{16} or C^{12}/C^{13} ratio from the ratio in an arbitrary standard substance.

$$\delta O^{18} = \left(\frac{R}{R_{std}} - 1 \right) \times 1000$$

where $R = O^{18}/O^{16}$ in sample

$R_{std} = O^{18}/O^{16}$ in standard

The oxygen standard is the oxygen of mean ocean water (Epstein and Mayeda, 1953). The carbon standard is the carbon of the Cretaceous belemnite as used by Urey and his colleagues at the University of Chicago. Calcite precipitated from sea water is enriched in 0^{18} relative to the sea water; to convert the oxygen values of the carbonates in this paper to the belemnite standard, subtract 30.0 from the δO^{18} given here relative to the mean ocean water standard (Clayton and Epstein, 1957).

All isotopic analyses have been corrected for mass spectrometer background and for mixing of sample and standard gases in the switching valve. The correction results in an increase of all isotopic differences by 4 per cent of the difference.

These samples are of three general genetic types of rock: (1) unaltered Leadville limestone, dolomite and chert (2), partly to wholly recrystallized limestone, dolomite and chert at and very near incipient or very small-scale hydrothermal dolomitization and sulfide mineralization, and (3) sample of hydrothermal dolomite silica and calcite from the large, intensively dolomitized halo around ore at Gilman. Most of the samples of type 2 were obtained on the west and southeast slopes of the Sawatch range, at Taylor Pass, Fulford and Trout Creek (Fig. 1, Table 1). Specimens of type 3 are from the periphery of the dolomite mass, at Minturn and Bolts Lake, and wherever feasible between these points and the ore body at Gilman. Samples were taken from areas where the simplest geological relations seem to exist. Those judged most characteristic of the rocks in question on the basis of field and petrographic examination were selected for analysis. The basic objective throughout the analytical work was to determine the isotopic compositions of oxygen and carbon from rocks whose geological origin seemed best understood.

ISOTOPIC COMPOSITION OF OXYGEN IN THE SAMPLES

It is known that isotopic composition of carbonates and silica which precipitate slowly, under equilibrium conditions, from a water solution, have values that depend on the isotopic composition of the water and the temperature of precipitation (Urey 1947; Urey *et al.*, 1951; Silverman, 1951). It can be expected, therefore, that the oxygen of the "unaltered" Leadville limestones, cherts, and dolomites, when invaded by an abundance of hydrothermal solution, will be exchanged with the solution. The $0^{18}/0^{16}$ ratio of carbonates and silica can be expected to assume values depending upon the isotopic composition of the oxygen of the hydrothermal fluids and upon the temperature at the time of the isotopic exchange.

The ratio of $0^{18}/0^{16}$ ratios between any oxygen compounds which are coprecipitated or recrystallized together in equilibruim in the presence of the hydrothermal fluid depends upon temperature only. Generally, the higher the temperature at wich the different coexisting phases have formed the smaller the ratio of the $0^{18}/0^{16}$ ratios of the different phases. In addition, both carbonates and silica seem to have $0^{18}/0^{16}$ ratios some 30 to 40 per mil greater than that of the natural waters from wich they are precipitated at room temperatures; therefore, the higher the temperature of equilibration between the various phases the lower should be the $0^{18}/0^{16}$ ratio relative to that of the involved water [1].

Work on pairs of dolomite and quartz from the Leadville indicate there is no measurable fractionation between these coexisting phases. Consequently our conclusions concerning relative temperatures of formation of various samples are based principally upon the analyses of quartz-calcite pairs. These are present in the form of limestone and chert throughout the unaltered Leadville limestone, and at sites with jaspery silica. Only one quartz-calcite pair seemingly formed in equilibrium could be found at the ore in the large bodies of hydrothermal dolomite for use as a relative temperature indicator at this point. The reliability of this single measurement is enhanced by the fact that essentially between the O^{18}/O^{16} ratio of each mineral and that of the per mil difference of what texturally seem to be coprecipitated dolomite and quartz at the ore. These last stated facts would seem to indicate the attainment of isotopic equilibrium between the closely associated quartz, calcite and dolomite. Similarly, the chert-dolomite pairs in what are readily inferred from regional field relations to be diagenic dolomites have approximately the same $\delta\ 0^{18}/0^{16}$ values as the quartz in the chert-calcite pairs in closely associated, unaltered cherty limestone. Here also, there appears to be good evidence of oxygen isotope equilibrium between these different, closely associated mineral phases in the hydrothermal unaltered parts of the Leadville formation.

The relations encountered suggest therefore the following generalization: in the Leadville formation, wherever there is good field and textural evidence for chemical equilibrium between the oxygen-bearing minerals a relationship exists between the $0^{18}/0^{16}$ ratio of each mineral and that of the per mil difference between the O^{18}/O^{16} ratio of different mineral. The greater the δ values of each mineral (quartz, calcite, dolomite) the greater the diffrences in the δ values of coexisting quartz-calcite or dolomite-calcite pairs. This must mean that the δ value of each mineral is sensitive to temperature—the δ value decreasing with increasing temperature. This also suggests that there was a large amount

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[1] For elaboration of the relationships between the $0^{18}/0^{16}$ ratio of calcite, quartz and dolomite see the companion paper (Clayton and Epstein, 1957).

of hydrothermal fluil of relatively uniform oxygen isotope composition in contact with the coarsely crystalline dolomite, quartz and calcite during their formation. It should be emphasized that, if an isotopic gradient existed in the hydrothermal fluid permeating the Leadville formation, this gradient would seem to have been relatively small compared to the $0^{18}/0^{16}$ gradient in the minerals as determined by temperature [2]:

Integration of the geological relations and oxygen isotope data in the investigated hydrothermally altered Leadville suggests that the δ values for any one of the coarse-grained, intergrown minerals —calcite, dolomite or quartz— may be used as a temperature indicator when coexisting mineral pairs are not available. Clearly this conclusion is confined to the parts of the hydrothermal aureoles investigated in detail, and seems warranted only because of the remarkable consistency between the oxygen isotope analyses and the existing geologic evidence. There are obvious pitfalls in a more general use of the $\delta\ O^{18}/O^{16}$ values for single minerals for purposes of relative temperature determination.

In the following pages the relationships between the field data and the isotope analyses are noted and related more specifically.

SAMPLES OF UNALTERED LEADVILLE FORMATION

The calcite-chert pairs LV86A, 86B, 86C and LV267. 274C and 274S, were chosen on the basis of field studies as typical of the inferred least altered limestone and chert from the cherty zone 2 of the Leadville formation (Figure 2). The oxygen in the unaltered limestone and cherts is the highest in 0^{18} of any oxygen from calcite and quartz that we analyzed, and for each mineral species the composition of the oxygen appears to be quite uniform irrespective of texture stratigraphic position or locality.

The well-defined fractionation between the δ°/oo[3] of oxygen in the limestone and the immediately associated chert (approximately δ°/oo of 6 to 6.5) appears to represent the equilibrium isotopic fractionation between these mineral pairs at near surface temperature in the presence of abundant water (see Clayton and Epstein, 1958). It is notable that the only calcite-quartz pair (L4) found in the hydrothermal halo, at Gilman ore, gives the lowest $\delta\ 0^{18}$ values

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[2] The inferred relationships between the δ values for calcite, dolomite and quartz minerals are more fully discussed by Clayton and Epstein (1958).

[3] °/oo is the symbol used for "per mil" and the δ°/oo (or δ alone) is read "deviation per mil" or simply "delta".

found in any samples of these minerals (calcite δO^{18} = 13.4, quartz δO^{18} = 16.1). These are indicative of much higher temperatures of formation than the calcite-quartz pairs at the periphery of the halo, and those in the unaltered beds (Table 1).

The dolomite-chert pairs LV504D, LV504S and LV510D and 510S are inferred from their field relations to be either sedimentary or diagenic in origin. Consequently they are thought to reflect the same conditions of exchange as the calcite-chert samples LV86A, LV86B, LV86C and LV267. The oxygen isotope compositions obtained are consistent with and seem to fortify this interpretation. The values for the cherts in the dolomite are essentially the same as those obtained for the cherts in the limestones (Table 1). It is apparent that the dolomites have essentially the same δ values as the cherts. As already note this absence of measurable fractionation exists in all of our samples of dolomite and quartz that are inferred from geological data to have formed in equilibrium with excess water (Table 1; see also Clayton and Epstein, 1958).

SAMPLES FROM AREAS OF INCIPIENT HYDROTHERMAL ALTERATION

The samples LV3A, LV3B, LV3C and LV211 are of Leadville limestone that is megascopically and microscopically almost identical with the unaltered limestone (LV86, LV267), but represents beds weakly altered and only partly replaced by hydrothermal dolomite, most of witch occurs along visible fractures. All of these samples were obtained within a few inches to 25 feet from narrow veins and irregular apophyses of hydrothermal dolomite and associated weak sulfide mineralization.

The dolomites LV210 and LV547 are from the same type of occurrence and are inferred from geological features to represent the weakest manifestations of hydrothermal dolomitization.

It is apparent that the microcrystalline limestone analyzed from these localities of incipient hydrothermal alteration (LV3A, LV3A, LV3C) show littlé if any change in oxygen isotope composition from similar looking samples of unaltered Rock (LV86A, 86B) that are one or more thousands of feet from known hydrothermal alteration. In contrast the field relations as well as the decrease in $\delta O^{18}/^{16}$ for the recrystallized calcite LV2A, LV2B, LV546, suggest that the calcites have under-gone marked exchange with hydrothermal waters. This suggestion is borne out by oxygen isotope analysis of quartz that occurs with LV2B. The quartz has a δO^{18} value of 22.2 which indicates this quartz-calcite pair has undergone extensive isotopic exchange with the hydrothermal solutions.

active at that site. In this respect the $\delta O^{18}/O^{16}$ value of sample LV547 also is of interest. This is the hydrothermal looking dolomite mass that envelopes LV546, and cuts discordantly across nearby beds of calcite limestone. The δ O^{18}/O^{16} value of dolomite LV547 is 4.2 greater than that of the associated recrfstallized calcite (LV546), an amount expectable if these minerals have undergone essentially complete exchange with abundant, identical waters. All of these specimens are from small veins of sulfides in peripheral areas of mineralization. A clear-cut correlation exists between visual evidence of recrystallization in these samples and an oxygen content lower in o 0^{18} than in "unaltered" samples.

SAMPLES FROM THE GILMAN-MINTURN AREA OF INTENSE HYDROTHERMAL ALTERATION

The very large pervasively dolomitized mass of limestone in the Leadville formation at and near the Gilman, Colorado ore body was chosen as the source of carbonates and silica formed by intense hydrothermal processes. Calcite is very rare. Only one sample containing calcite and coexisting quartz was found. Fortunately, this single calcite-quartz pair occurs at the Gilman ore body (L4 and L4S). Samples of the several types of hydrothermal dolomite were taken. however, as follows: (1) at and near the exposed periphery of the hydrothermal dolomite mass, near Minturn, Colorado, (2) at intervals across the hydrothermal dolomite mass from its periphery to the very contact with the major segments of the Gilman ore body. This represents a distance of approximately 2 miles along the strike. In addition, through the kind cooperation of the management at Gilman, samples of dolomitized and silicified Leadville formation also were obtained from drill cores at distances of tens to several thousands of feet, north east, and southeast of the Gilman ore body. The nearest known major ore body is that at Gilman, but it is impossible to disprove the existence of unknown ore much closer to these holes.

Textures and related lithologic features proved to be excellent guides to the degree of isotopic exchange of oxygen. The Pink Breccia, and waxy bed (Fig. 2, Table 1) that remained fine grained and dense during the entire process of hydrothemal dolomitization show far less exchange than the coarse white dolomite in crystals that line vugs in zebra rock of the Upper Leadville. Similarly, dense microcrystalline cores of chert nodules in the hydrothermal dolomites show little or no exchange compared to the bleached and recrystallized rims.

Because the textures of the hydrothermal dolomites are influenced by primary features, there was, in a sense, marked stratigraphic control of oxygen isotope exchange during alteration of the Leadville limestone. Wherever feasible at each locality samples were obtained from the following sources: (1) waxy bed, at the base of the middle member; (2) dark medium-grained dolomite and associated chert in the middle member; (3) pink breccia at the base of the upper member; (4) zebra rock (both dark finer-grained matrix and coarse white crystals with associated quartz crystals). [4]

The analyses of zebritic dolomite and associated quartz will be discussed first. The oxygen isotope values of these samples have been plotted on Figure 3 according to textural type. oxygen isotope composition and distance from known ore. The samples of this type from peripheral parts of the hydrothermal dolomite, or from at least 1 mile distant from known ore, include the pairs LV403 and LV411 and LV196D and LV196x1. These represent two pairs of samples from two peripheral localities. Each pair (Table 1) consists of medium-grained dark dense dolomite and coarse white crystals. For example, LV403 is the dark dense dolomite phase and LV411 the associated white crystals in zebritic dolomite about 10,000 feet southeast of the known ore at Gilman, Colorado. LV196d and LV196x1 are respectively dark dense and associated coarse white crystalline dolomite some 10,000 feet north of ore at Gilman.

In each pair of samples the finer-grained, dark-colored dolomite has a greater $0^{18}/0^{16}$ ratio than the white crystals. Presumably the oxygen of the white crystals was completely exchanged with that in the hydrothermal solutions that induced its recrystallization. It is interesting to note that the dolomite crystals on the periphery of the major dolomite mass show oxygen isotope values approximately the same as those from the smaller, outlying sites of dolomitization and mineralization. The range in values in the slightly altered rocks (LV210, LV547, LV403, LV411, LV196) is from δ23.8 to 20.1. It should be noted that the coarser crystalline fraction of LV196 was contaminated with finer-grained material, hence the $\delta O^{18}/O^{16}$ value for pure, coarse crystals from the Bolts Lake locality may be lower than 23.3. In any event, the analyses to date suggest that for the periphery of the large Leadville-Gilman mass of hydrothermal dolomite in the Leadville and Gilman area, and for the widely scattered small masses of hydrothermal dolomite the mean value of $\delta 0^{18}/O^{16}$ is somewhere in the interval of δ20.0-22.0.

Samples of zebritic dolomite and associated quartz obtained at distances of 500 to 4,000 feet from ore include LV824d, and 824x1, LV573d, LV571d, LV571x1, LV561x1 and possibly LV563. The correlation between texture of dolomite and composition of oxygen holds here also. The specimens of white crystals, LV561x1, LV824x1, LV571x1 and of the medium-grained LV573d

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[4] Not all of the quartz crystals were analyzed after it was found that there was no appreciable isotopic fractionation between quartz and the coarsely crystalline white dolomite.

contain distinctly lower $\delta O^{18}/^{16}$ values than in the dolomite at the periphery of the hydrothermal halo. A $\delta O^{18}/O^{16}$ value of between 19.5 and 18.0 is indicated. The specimens of coarsely crystalline dolomite at and within 100 feet of the ore body at Gilman (LV7x1, LV567, LV831, LV825x1, LV569x1) appear to have mean composition of $\delta O^{18}/O^{16}$ of about 17.0 with a known lower limit (LV569 x 1) of $\delta = 16.4$ (Table 1 and Figure 3).

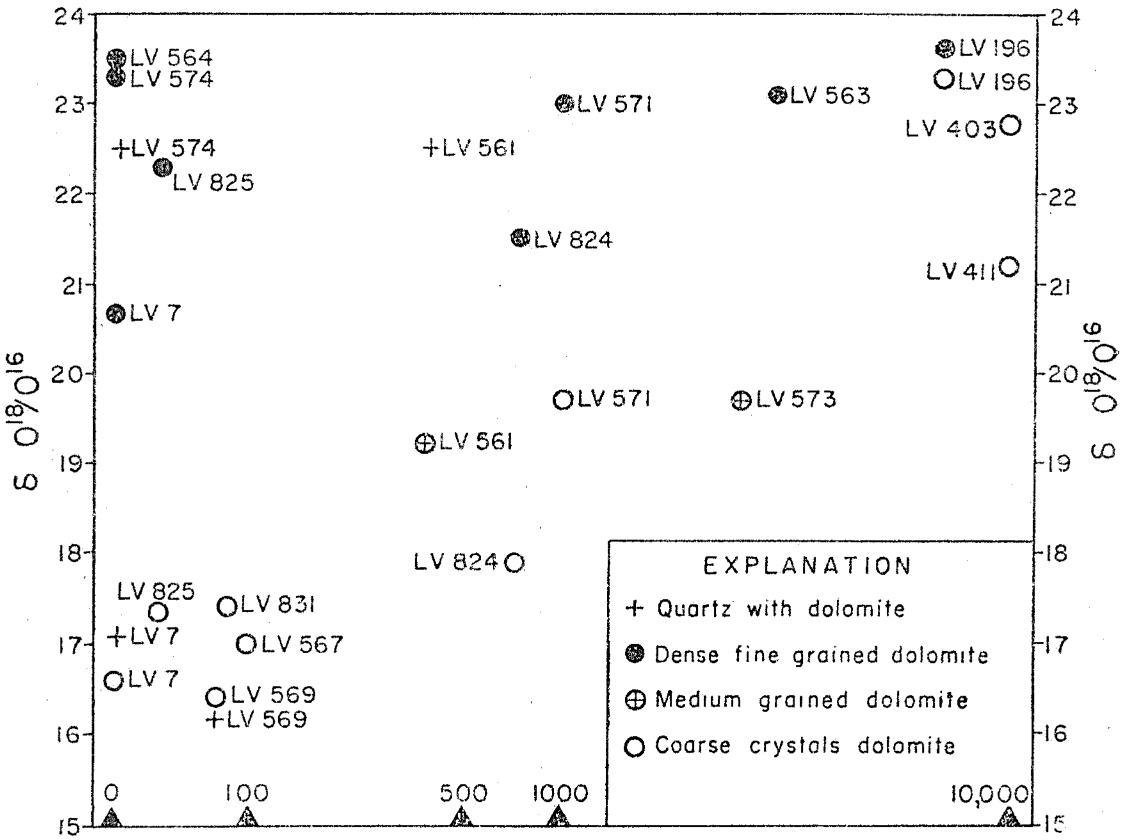

Fig. 3. Graph of the relations between texture, oxygen isotope composition and distance of samples of hydrothermal dolomite from ore at Gilman, Colorado.

These values strongly suggest a decrease in the O^{18} composition of the oxygen in the coarse crystals of dolomite and in quartz and in the rare calcite as the major Gilman ore body is approached. Presumably these differences reflect a temperature gradient outward away from the site of ore, at the time the dolomite formed.

Systematic differences in isotope composition of oxygen in the hyrothermal dolomite definitely appear to be confined, however, to the coarse white crystals in the zebritic dolomite. There appear to be no marked, systematic differences in the dark-colored, finergrained dolomite intimately associated with the crystals (Table 1 and Fig. 3).

The analyzed specimens of waxy bed and pink breccia offer two other examples of seeming correlations between lithology, proximity to ore and isotopic composition of oxygen. The dolomite specimens from the waxy bed are grouped together in Table 1 (LV109, 149, 362, 192, 404, 406, 334, 200, 57) in approximate order as determined by distance from intense centers of hydrothermal activity. The specimens from the pink breccia at the base of the upper member (LV359, 175, 179, 181, 61, 43, 41 and 54) are similarly grouped. With the exception of one aberrant value in each suite there is no doubt of a general decrease in 0^{18} composition of oxygen in those specimens near and at sites of intense hydrothermal dolomitization and sulfide mineralization. In each of these examples the oxygen isotope compositions seem to reflect gradients in temperature, in the Leadville, during isotope exchange.

The single obviously inconsistent value for each of the two rock types (LV57 and LV61) is, interestingly enough, from the same locality. The specimens LV57 an LV61 represent respectively waxy bed and the base of the upper member in barren dolomite some 1000 feet from ore in the Gilman mine. Considering the proximity of these specimens to the Gilman ore body they both might be expected to have δ values at least 2.0 lower than recorded.

Two of the outstanding features of the analyses of these groups are the consistency of the values of oxygen and carbon, and also the well-defined differences between δO values for different rocks types from the same locality.

It does not seem possible at present to make any detailed interpretation of the carbon isotope analyses. Generally the "unaltered" calcite limestones and the "diagenetic" dolomites (LV504, LV510 and all specimens from the "waxy bed") have δC^{13} about zero, that a $C^{13}/^{12}$ ratio equal to that of our standard, which is a sedimentary calcite. The average of the dark dense dolomite is lower in C^{13}, giving a $\delta C^{13}/C^{12}$ of -3.5%, while the "pink breccia" is very uniform, averaging -5.2%.

In the specimens where the dark and light parts of the zebritic dolomite have been analyzed, the white crystals are generally richer in C^{13} by obout 0.5%.

An understanding of the significance of the variation in C^{13}/C^{12} rations in some instances, and of the homogeneity of the ratio in others, must await detailed study of the isotopic fractionation of carbon among carbonates and aqueous solutions at high temperatures.

SUMMARY AND CONCLUSIONS

The analyses of the oxygen isotopes 0^{18} and 0^{16} in unaltered and hydrothermally altered limestone, dolomite and quartz show a range in δ value as follows:

mineral	range of δ 0^{18}
calcite	24.1 ←→ 13.4
dolomite	28.6 ←→ 16.4
quartz	30.4 ←→ 16.1

The highest $\delta O^{18}/O^{16}$ values are obtained from bedded calcite, dolomite and chert which have not been recrystallized by hydrothermal water ("unaltered" beds). The lowest $\delta O^{18}/O^{16}$ values are from the hydrothermal calcite, dolomite and quartz closest to ore which therefore appear to have been recrystallized at highest temperatures. These variations in the oxygen isotope composition are consistent with independent geological evidence of the origin of the rock.

In the unaltered beds $\delta O^{18}/O^{16}$ values appear to vary little for a given carbonate or for quartz along or across bedding. They differ by some -6.0% from the values in carbonate or silica laid down in isotopic equilibrium with ocean water. This difference as well as the uniformity in values may be the result of extensive isotope exchange of the original sedimentary constituents with connate or ground waters during or after initial lithification of the rock.

The extent of the oxygen isotope exchange induced by hydrothermal waters appears dependent upon the temperature at the time of exchange, the kind and amount of hydrothermal water present and the degree to which exchange could take place between the water and the recrystallizing or newly forming phase.

Generally the isotopic analyses of a single mineral at a locality, will not show that the mineral was in isotopic equilibrium with its surroundings at the time recrystallization. If two or more minerals from the same specimen are analyzed, some conclusion can be drawn concerning their equilibration with one another and with their environment. This point has been discussed in preceeding pages with relation to the quartz —calcite system and by Clayton and Epstein (1958). In the parts of the Leadville formation investigated, the δ values for the crystalline minerals quartz, dolomite and rare calcite, and between dolomite and calcite, are consistent with agradient of temperature between the ore and the margin of the hydrothermal dolomite. Both the δvalue and the difference in δ values decrease with increased temperature.

Abrupt and marked variations in texture of carbonates or quartz are commonly accompanied by sympathetic variations in composition of associated oxygen. Invariably the lowest δO^{18} values occur in those grains of the mineral that appear to have undergone most extensive recrystallization in contact with abundant hydrothermal water. Thus, the coarse crystals of white dolomite that line vugs in the zebra rock are consistently lower in δO^{18} than the associated dark, medium grained matrix dolomite. This medium-grained dolomite is in turn lower in δO^{18} content than the very dense, microcrystalline waxy bed a few feet away.

Similarly, quartz crystals growing on chert at sites of marked hydrothermal alteration are lower in δO^{18} than the incipiently to moderately recrystallized rims of the chert nodules. These rims of the chert was in turn lower in δO^{18} than the bleached but still dense microcrystalline cores of the nodules.

The effect of time and temperature of crystal growth appears to be especially apparent in the oxygen isotope values from the multitextured zebritic dolomite. There the paragenesis is: dark medium crystalline dolomite coarse white crystals dolomite sand. The data in Table 1 show that the above sequence is paralleled by a decrease in δO^{18} for these several types. Moreover, for any given locality and textural type, very similar δO^{18} of quartz associated with each of these types of dolomite (Table 1).

If the above possibilities are correct several interesting implications may be noted. One is that isotopically as well as texturally each preceding type of dolomite represents an unstable relict which did not exchange oxygen appreciably with the waters involved in the growth of successive textural types.

A second implication is that either no obvious temperature gradient existed in the hydrothermal dolomite when the dark medium grained dolomite was formed, or else a relatively small amount of water was involved. On the other hand a temperature gradient seems to have existed when the coarse white crysta slgrew. The basis for this second conclusion is apparent in Figure 3, where the textural types of dolomite composing zebra rock are distinguished and their oxygen compositions plotted against distance from known, large bodies of ore.

The crudely systematic decrease in δO^{18} compositions of the coarse white crystals from the periphery of the dolomite halo to the site of the Gilman ore deposit (see also Figure 2) is especially note worthy. This relation suggests that the white crystals grew in the presence of hydrothermal solutions that entered the Leadville at and near the present ore. The outward spread of these solutions, in the Gilman area, appears to have been as fairly uniform wave involving loss of heat. The data are consistent with the idea that both the dolomitizing and ore-forming solutions entered the Leadville via the same major channel or chanels at or near the present site of ore.

The temperature gradients indicated by the oxygen isotope data in the coarse white dolomite may be analogous in formn and direction with those extant during during the subsequent emplacement of ore; but the temperature gradients of the two processes need not have been identical. Of all the dolomite types, the sanded zebra rock appears to have formed most nearly at the same time as ore. Unfortunately this dolomite sand may be too soptty in its distribution away from ore to be used in detailed tests of temperatures and temperature gradients in the entire dolomite halo.

The trends noted above in the isotopic composition of oxygen in the hydrothermal dolomite are not reflected in the concentration of constituent elements. For example, detailed studies[5] of the amounts of Cu, Pb, Zn, Mn, Sr, Ti, Al, and other elements in the dolomite indicate no systematic trends with respect to ore, inferred ore conduits or other features. In fact the recorded differences of $0^{18}/0^{16}$ from the margins of hydrothermal dolomite to ore contacts appear to be the one known chemical property of the hydrothermal dolomite that may prove useful as a guide to ore.

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EXPLORACIÓN GEOQUÍMICA DE LA SIERRA DE GUADARRAMA (ESPAÑA)

F. DE PEDRO HERRERA *

RESUMEN

Constituida en su totalidad por granitos recubiertos en diversos puntos por una cobertera gneísica, especialmente en su parte N, ha sido sometida a una rigurosa exploración geoquímica de sus rocas, analizando 260 ejemplares con un volumen de datos que supera a los 4,000 valores; dándose en este trabajo un resumen de las investigaciones y las principales conclusiones.

Por las características macroscópicas se diferencian una serie de grupos de rocas que responden a composiciones distintas, apareciendo como más pobres en elementos menores las de grano muy grueso y homogéneo, mientras que las de grano medio se asemejan progresivamente a las rocas gneísicas.

Las consideraciones sobre los fenómenos observados, conducen a la conclusión de haberse formado las rocas de esta Sierra en el fondo de un geosinclinal precámbrico, con gran movilidad de los elementos habiendo tenido lugar una serie de migraciones para acomodar los materiales originales a las condiciones energéticas reinantes.

Con este criterio se distinguen una serie de bloques de origen tectónico con distinta concentración de elementos, apareciendo limitados por discontinuidades geoquímicas.

Las concentraciones de posible interés minero son escasas, y aparecen encajadas en rocas más pobres en tales elementos, por regla general, que la media total de su grupo, como resultado de concentraciones por diferenciación en estado sólido.

INTRODUCCION

En esta zona de 5.000 Km^2, con altitudes entre 700 y 2.400 m, situada en el centro de España y formada por rocas graníticas y gneísicas, el autor de esta síntesis ha realizado una intensa exploración geoquímica, aplicando los criterios de:

— contenido en elementos mayores y menores, de los distintos tipos de rocas

— distribución en la topografía guadarrameña

investigando la:

— relación entre unas rocas y otras, por los fenómenos de tránsito o contacto

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— localización de las unidades estructurales
con objeto de establecer:
— esquema de evolución
— conclusiones teóricas y prácticas.

Contenido en elementos de los distintos tipos de rocas. Se han investigado con preferencia los elementos menores, empleando técnica espectroquímica semicuantitativa de capa catódica con lente esferocilíndrica e imagen fraccionada ( ), en espectrógrafo Hilger E2 de gran dispersión, en la zona comprendida entre 8.000 y 2.463 A; comparando con los patrones de concentración dando a x valores enteros de 0 a 8, y con error menor de un tercio de escalón.

Las cantidades de elementos mayores se han obtenido por técnicas gravimétricas y espectrofotocolorimétricas, clásicas en análisis químico; habiendo incluido en estos valores los aparecidos en la bibliografía de otros autores, después de transformar sus números en partes por millón (ppm) del elemento considerado.

Para el oxígeno se ha seguido el criterio de considerar el correspondiente a la estequiometría de los elementos más abundantes, despreciando el de pocas p.p.m. por estar ya incluido en los anteriores, dado el carácter de las determinaciones analíticas ordinarias, sin que las pequeñas diferencias en valencia tengan ninguna significación.

Los grupos se han confeccionado a partir de las características macroscópicas, habiéndose encontrado que a pesar de haber muchos términos intermedios, pueden diferenciarse unos cuantos tipos que geoquímicamente están perfectamente definidos:

Ga	Granito aplítico o de grano fino, pocos elementos micáceos; muchas veces se forma en zonas de fracturas visibles o determinables; representado en ocasiones por verdaderas aplitas.
Gg	Granito de grano grueso, muy homogéneo, es biotítico y no contiene apenas gabarros, sus pegmatitas son pequeñas y difusas; forma grandes lisos en el terreno, en una topografía muy accidentada, destacando por formar sierras características sin vegetación.
Ggp	Se ven grandes cristales difusos, muchas veces orientados; casi siempre en cercanías de gneiss, muy glandular, se localiza a media ladera y algún fondo de valle.
Gm	Lo denominaremos granito de grano medio o normal, es el dominante y principal constituyente de la superficie de la Sierra, sobre todo de su zócalo marginal; es objeto de activa explotación para construcción; abundan los gabarros y en los contactos con rocas metamórficas hay enclaves de gneiss.

Gmp	Como el medio pero con existencia de fenocristales de plagioclasa, muchas veces orientados, parece una facies marginal del anterior.
B	Así se designan los negrones o gabarros que aparecen dentro de los granitos, fundamentalmente en el de grano medio. Son la escoria restante de los enclaves de gneiss englobados en proceso incompleto de granitización.
Rb	Grupo muy amplio donde se incluyen todas las rocas restantes más básicas que los granitos; gneiss, productos de transformación de éstos o algún lamprófido que representa el polo más básico de todas las rocas.
P	Rocas porfídicas en filones, de origen inseguro, pero que su diversidad en composición obliga a subdividirlas en dos: P1 y P2, según se expone en otra nota presentada en estas mismas sesiones.

Los datos obtenidos, prescindiendo de los elementos que por su homogeneidad en los valores no aportan ninguna luz para esclarecer los fines perseguidos, se han resumido en el Cuadro I, expresándolos en ppm del elemento y separando los dos grandes conjuntos de elementos mayores de los menores, dentro de los cuales se ha seguido el orden del potencial de ionización. Esta disposición nos permite distinguir perfectamente entre las rocas del dominio granítico y las que aún no han sufrido el proceso completo de granitización, pues aparece una ley según la cual existe un mínimo en el centro de los ocho elementos mayores con dos ramas crecientes en ambos sentidos, pero en la serie metamórfica en el sodio vuelve a aparecer otro, lo cual también sucede con el grupo P1 o sea los pórfidos incluidos en ella mientras que para las restantes se cumple perfectamente el aumento continuo hasta el potasio.

Dos polos opuestos se aprecian entre Ga y Rb, apareciendo prácticamente cambiados en sus apetencias por los distintos elementos. Las rocas graníticas son las de mayor contenido en oxígeno con una diferencia extraordinaria sobre los gneis, notándose bastante la influencia de las cuatro cargas positivas del ion silicio, pues decrece en el mismo orden que éste, siendo por tanto mucho menos cuarzosas las rocas metamórficas y sus productos de granitización incompleta, lo cual ya se sabía antes.

Los valores del aluminio dan para los granitos un valor menor, estando las mayores cantidades en los pórfidos y los gabarros, lo que se traduce mineralógicamente en la aparición de espinelas reconocibles al microscopio, en estas últimas rocas. Ambos grupos dan idea de que se han originado por lo menos parcialmente, por pérdida de otros elementos y aumento relativo de aluminio como más difícilmente migrante.

Los elementos hierro, magnesio y calcio, presentan un déficit extraordinario en los tipos más evolucionados y fuerte incremento en rocas metamórficas y demás denominadas básicas.

Respecto a los alcalinos, es distinto el comportamiento de sodio y potasio, mientras el primero presenta valores fluctuantes en un 10% en más o en menos, el segundo marca una diferencia tajante entre el dominio granítico y el resto de las rocas, resultando los gabarros los más desprovistos de él por su capacidad migratoria para engrosar el granito formante en los períodos petrogenéticos.

Los elementos menores se comportan mucho mejor, si cabe, de forma que salvo muy pocos valores anómalos y sin significación decisiva para este primer esquema, podemos decir que siguen la misma ley de hierro magnesio y calcio; todos disminuyen según se parte de las rocas metamórficas hacia los granitos más alejados, por lo que parece aceptable este sentido como el de la evolución.

Una anomalía parece introducir el rubidio, dando un mínimo muy acusado en los gabarros, y por el contrario un fuerte máximo en los granitos aplíticos, lo que forzosamente hay que relacionarlo con el comportamiento del potasio, elemento de potencial análogamente bajo, que a pequeñas distorsiones está energéticamente en posibilidad de migrar dada su pequeña apetencia electrónica, alejándose de zonas de competencia de otros cationes para buscar oxígenos más libres y abundantes. Si se pensara en que es un resto y los demás han podido salir y ellos no, entonces serían los predominantes en los gabarros dado el criterio que tenemos de formación de estas rocas tan particulares.

GEOQUIMICA DE LA TOPOGRAFIA GUADARRAMEÑA

Establecido el que unas rocas pueden derivar de las otras por reajustes químico-mineralógicos frente al campo energético en que se encuentran o son introducidas, se ha intentado establecer la existencia y características de esos niveles. El problema fundamental está en distinguir lo realizado por la tectónica tan intensa de este tipo de regiones y lo conseguido por los cambios químico-energéticos. La erosión por otra parte ha puesto al descubierto las distintas zonas y la labor principal ha sido correlacionar los datos de laboratorio con los de campo.

Así se ha visto que en los planos trazados con ayuda de los valores espectroquímicos, han salido unas agrupaciones perfectamente referidas al tipo de roca que domina en aquellos lugares, surgiendo discontinuidades tajantes, que a veces no tenían trazas de existencia en el terreno pero que junto con las visibles y también demostradas geoquímicamente dan un poligonado de la Sierra con delimitación de unos denominados bloques geoquímicos en principio, y que se ha visto tienen una realidad genética, de tal forma que ahora ha sido

CUADRO I

	I	Ga	Gg	Ggp	Gm	Gmp	B	Rb	Pl	P2
O	137,48	487600	481900	477600	482600	483900	462500	443000	461000	481000
Si	44,95	350200	341000	335000	341000	337000	290000	268000	303000	333000
Al	28,31	73500	71100	65500	71000	63000	80000	73000	78400	84200
Fe	16,24	7200	20000	23200	20000	30000	58000	74000	38700	14900
Mg	14,97	500	2000	4700	1800	6600	17000	27700	11600	1200
Ca	11,82	4000	12200	11700	11000	12400	33000	41000	23900	7800
Na	5,14	24600	24600	20000	18600	19100	12000	22400	18500	20700
K	4,34	44400	38500	40700	46000	33300	17000	25300	31400	47900
Ti	44,66	600	1500	2300	2550	2000	6300	6800	10000	1090
Zr	33,83	90	300	110	140	100	200	340	300	78
Cr	32,1	2	6	7	10	8	25	80	128	15
Cu	20,2	7	3	3	9	3	6	30	16	5
La	19,2	11	22	23	30	26	25	31	64	48
Be	18,14	2	2	2	1	4,5	3	6	1	1,5
Ni	18,13	1	2	2,5	1	5	5	24	27	4
Co	17,3	0	1	2	2	1	6	12	16	1
Mn	15,7	425	450	520	540	465	925	1080	1367	542
Sr	10,98	80	180	220	290	80	280	440	1172	330
Ba	10	560	490	520	600	560	380	1020	746	725
Li	5,39	100	130	140	120	100	160	320	201	183
Rb	4,18	450	470	535	410	450	535	490	333	582
Nº	rocas	27	43	19	67	12	30	22	32	

posible delimitarlos e incluso desplazarlos en la vertical para conseguir el esquema del geosinclinal en que se originaron estos granitos. Explicado así el por qué hacer mención especial del modo de aparecer cada tipo de granito diferenciado, tomemos el problema en conjunto y establezcamos:

— Los distintos tipos de rocas de la Sierra de Guadarrama se han originado en el fondo de un geosinclinal, por transformación de sus sedimentos.

— El aumento de la energía puesta en juego, según aumenta la profundidad, ha conducido en los casos más avanzados a una homogeneización de los materiales.

— Según se consideran granitos más profundos disminuye la cantidad de oxígeno, hierro, magnesio y calcio, aumentando en cambio la de silicio, sodio y potasio para un peso constante de roca.

— Los elementos menores son menos frecuentes con la profundidad, sufriendo un proceso análogo a una dilución.

— Los diques de lamprófido, pórfido, aplita, granitos aplíticos y zonas milonitizadas, son testigos de las roturas sufridas por el conjunto en los distintos períodos orogénicos desde la entrada de rocas básicas y posterior granitización incompleta, a simples recristalizaciones con diferenciación por migraciones de elementos químicos o persistencia de la cataclasis en períodos de menor energía.

— Estas discontinuidades y otras no visibles se ponen de manifiesto al hacer el estudio de la geoquímica regional, lo cual se marca perfectamente en la proyección de los valores cuantitativos en los planos del lugar.

— La intrusión de granitos profundos en otros más superiores, da lugar a zonas de fricción recristalizando en granitos más ácidos y aplíticos, tipo Ga, muy pobres en elementos menores dispersos, pero con un contenido elevado de oxígeno, silicio y alcalinos. A veces la concentración de otros elementos conduce a menas metálicas.

— Cuando aparece un granito pobre en elementos menores dentro de una zona de mayor concentración es signo de haberse formado menas metálicas en una diferenciación por concentración.

— Esto se debe muchas veces a las acciones mecánicas del desplazamiento de bloques, por roturas que han permitido la migración de elementos, respondiendo a sus características de potencial de ionización y radio iónico.

— Los contactos originados son bruscos, con inclusiones de gneis, o difusos con aparición de migmatitas y tránsito frecuente a granitos orientados.

— Los enclaves de gneis han evolucionado directamente a granito o, por concentración de elementos fémicos, originan gabarros, los que a su vez, por aporte cuarzo-alcalino pasan a granitos de grano medio.

— Vista la importancia de la diferenciación por concentración de elementos, y siendo muy escasos los valores aportados por las rocas originales para las concentraciones de éstos, hay que llegar a la conclusión de que en la Sierra del Guadarrama no habrá grandes concentraciones minerales con interés de explotación. Esto así sucede.

— Las zonas de granito de grano grueso serán las menos propicias para los yacimientos, los cuales se tendrán que buscar en los granitos de menor energía, los de abundantes gabarros, y dentro de ellos buscar las zonas de fractura que hayan permitido la concentrción con empobrecimiento de las inmediaciones. Pero como decimos, tampoco serán de gran interés y se agotarán pronto difuminándose en la roca encajante, con un mínimo de concentración en ésta, valor dependiente del coeficiente de difusión y después lejos del dique habrá la concentración correspondiente al tipo de roca.

НОВОЕ В ГЕОХИМИИ ОЛОВА

В. Л. Барсуков

ABSTRACT

1—Varieties of "no-tin bearing granites" not altered by postmagmatic processes and contact-action contain a tin amount of 3-5 r/t, corresponding to its clarke, while "tin bearing granites" contain 16-30 r/t of tin.

2—80-100% of the tin included in granite is concentrated in biotites and enters isomorphously into their lattice on the place of Fe^{+3}. Biotite is the only mineral-concentrator of tin among the rock forming minerals, and its Sn content indicates the tin content of the granite.

3—It has been ascertained that in the process of muscovitization of biotite which accompanies the granite albitization, the tin included in biotite is expelled from the crystalline lattice of mica and changes to an infiltrating alkaline postmagmatic solution.

4—In a number of tin deposits of a quartz-cassiterite formation, the existence of a vertical zonality is displayed by the various characters of the wall rock alterations.

5—In agreement with the chemical interpretation of the observed vertical zonality and the laboratory investigations we draw the conclusion that this zonality may not be explained from the view-point of Daubrée's theory, but that it is quite in conformity with the hypothesis suggested by us of a tin transfer in the form of a compound of the Na_2 [Sn (OH, F)] type.

6—It has been stated that the upper ore-bearing zone is characterized by a systematic decrease of the tin content in the host rocks with increasing distance from the gangue up to a normal Sn content in the tin bearing granites. The lower sub-ore zone is characterized by the presence of a vast zone of tin outcarrying from the host granites; that agrees with the idea of origin of ore substance, the forms of its transport and the conditions of migration and concentration.

До последнего времени вопрос о том, существует ли различие в содержаниях и распределении олова в гранитных массивах, несущих и не несущих оловянное оруденение, оставался не выясненным. Неясным также оставалось первичное распределение олова в гранитоидных породах и его поведение при постмагматических гидротермальных изменениях пород.

Проведенными работами выяснено, что гранитные массивы, не несущие оловянного оруденения (хотя ни по возрасту, ни по минералогическому составу они существенно не отличаются от "оловоносных гранитов"), содержат олово в количестве 3-5 г/т, что соответствует его кларку. Массивы, несущие оловянное оруденение в разностях, не измененных постмагматическими и приконтактовыми процессами, содержат олово в несколько раз (до 4-5 раз) больших количествах, чем его кларк: 16-30 г/т (обычно 18-26 г/т). Следовательно, в случае "оловоносных гранитов" можно говорить об обогащении оловом гранитной магмы, из которой сформировалась данная интрузия, т.е. говорить о специализации этой гранитной магмы.

"Оловоносные граниты" характеризуются повышенным содержанием олова в своих разностях, не измененных ни контактовыми ни постмагматическими процессами. Гранодиоритовые зоны вокруг гранитного массива, образовавшегося в результате ассимиляции гранитной магмой вмещающих песчано-сланцевых пород, обеднены оловом. В них содержание олова падает до 3-5 г/т. Вмещающие песчано-сланцевые породы у контакта с "оловоносными гранитами", наоборот, обогащены оловом, причем, содержание в них олова уменьшается при удалении от контакта с гранитами от 15-25 г/т до 5-6 г/т, т.е. до кларковых количеств. Все это говорит о том, что источник олова, фиксирующегося в гранитах, магматический.

Но далеко не все минералы, кристаллизующиеся из гранитной магмы, обогащенной оловом, несут на себе следы этой специализации магмы. Так, из всех породообразующих минералов неизмененных разностей гранита (см. табл. № 1), единственным "минералом – концентратором" олова является биотит.

Кварц – полевошпатовая часть гранита практически не содержит олова, и 80-100% олова, заключенного в неизмененных разностях гранита, сосредоточено в биотитах. Содержание Sn в биотитах, достаточно близкие в различных участках "оловоносного гранита" и колеблются от 80-100 г/т до 300-400 г/т Sn, тогда как в "неоловоносных гранитах" содержание олова в биотитах не превышает 30-50 г/т. Таким образом, биотит является наиболее чувствительным из породообразующих минералов, который отражает общую первичную оловоносность магматического очала, и является "индикатором" оловоносности гранита.

Акцессорный касситерит в неизмененных постмагматическими процессами гранитах нигде не был обнаружен. Кристаллохимический расчет возможности изоморфного вхождения олова в кристаллическую решетку биотита показал, что оно может находиться в углах кристаллической решетки биотита.

Вхождение Sn в эту решетку может осуществляться путем двуступенчатого изоморфизма:

$$\mathrm{Li}^{+1}\ \mathrm{Fe}^{+3} \longrightarrow \mathrm{Mg}^{+2}\ \mathrm{Fe}^{+2}$$

и

$$\mathrm{Li}^{+1}\ \mathrm{Sn}^{+4} \longrightarrow \mathrm{Mg}^{+2}\ \mathrm{Fe}^{+3}$$

При таком изоморфизме компесация зарядов достигается параллельным "допущением" в решетку лития. Радиусы ионов Li^{+1} и Mg^{+2} соответственно равны 0,78 Å, а по строению своих электронных оболочек оба иона относятся к одной группе ионов, типа благородных газов, что обусловливает достаточно совершенный изоморфизм между ними.

Совершенность изоморфизма Fe^{+3} и Fe^{+2} общеизвестно и не требует специального рассмотрения. Радиусы ионов Sn^{+4} и Fe^{+3} почти одинаковы и равны 0,74 Å и 0,67 Å. По строению своих электронных оболочек ионы Sn^{+4} и Fe^{+3} принадлежат к разным группам. Ион Sn^{+4} имеет 18-ти электронную внешнюю оболочку, т.е. построен по типу ионов "купро", тогда как ион Fe^{+3} имеет внешнюю оболочку из $8 \div 5$ электронов, и принадлежит к группе ионов промежуточного типа, с достраивающейся третьей оболочкой. Близость кристаллохимических свойств обусловливает возможность изоморфизма между ними. Суммарный выигрыш энергии при таком изоморфизме определяется (по расчету)в 844 ккал/моль.

Для того, чтобы убедиться в правильности предположения об изоморфном вхождении олова в решетку биотита, ряд мономинеральных фракций биотита, истертых до 200-300 меш. были подвергнуты тридцатиминутному центрофугированию в иодистом метилене. Результаты количественного спектрального анализа проб до и после центрофугирования показаны в таблице 2.

Таблица 2

№№ проб	152	156	263	170	224	120	103
Содержание Sn в биотите в г/т до центрофугирования	30	30	30	43	80	240	310
Содержание Sn в биотите в г/т после центрофугирования	30	30	30	43	80	210	310

Как видно из приведенных данных, никакого уменьшения содержания Sn в биотитах после центрофугирования не наблюдается, даже в случае максимальных содержаний 300 г/т Sn. Следовательно, олово действительно входит изоморфно в решетку биотита, не образуя самостоятельного минерала касситерита, рассеянного по спайности слюды, т.к. в этом случае наблюдалось бы уменьшение содержание олова после центрофугирования.

Постмагматические автометасоматические изменения гранитов, обычно, выражаются в альбитизации полевых шпатов и мусковитизации биотита, причем второе является следствием первого. Кристаллохимически мусковитизацяи биотита сводится к замещению в шестерной координации Fe^{+2} и Mg^{+2} трехвалентными ионами Al^{+3} и Fe^{+3}. Кристаллохимический расчет показывает, что при вхождении в решетку Al^{+3}, одновременно с вытеснением Fe^{+2} и, частично, Mg^{+2} будет вытесняться и Sn^{+4}.

В таком случае, олово обнаруживаемое в мусковитах должно находиться в виде субмикроскопического акцессорного касситерита, рассеянного по спайности слюды.

Приведенные в таблице № 3 результаты определения содержаний Sn в мусковитах до и после центрофугирования растертых до 250 меш. мономинеральных фракций показывают, что действительно, независимо от общего содержания олова в мусковите, большая его часть находится в виде акцессорного касситерита, и лишь в незначительных количествах (~ 20 г/т Sn), возможно остается изоморфно связанным в решетке мусковита.

Таблица 3

№№ проб	145	150	237	151	142	172	144	120	101	102	119	105
Содержание Sn в г/т в мусковите до центроф.	19	20	26	81	98	115	170	220	230	300	500	1000
Содержание Sn в г/т в мусковите после центровугиров.	19	20	17	36	83	65	140	110	180	170	260	500

Следовательно, значительная часть олова, первоначально изоморфно заключенного в биотите, при мусковитизации последнего должна вытесняться из кристаллической решетки слюды и переходить в просачивающийся щелочной постмагматический раствор.

Таблица 4

Наименование породы	Двуслюдяные и мусковитовые граниты											Грейзенизированные граниты			
	(Среднее содержание олова в неизмененных гранитах — 27 г/т)														
№№ проб	103	115	120	142	145	150	172	237	151	144	149	102	101	105	119
Общее содержание Sn в г/т	19	16	23	7	9	<3	18	7	4	10	13	57	78	207	31
Содержание Sn в биотитах в г/т	310	60	250	170	190	110	250	38	—	—	—	—	—	—	100
Содержание Sn в мусковитах в г/т	200	43	220	98	19	20	115	26	81	170	—	300	230	1000	500

Частично оно здесь же выпадает в виде акцессорного касситерита, но в значительной степени выносится щелочными растворами в вышележащие горизонты. Такие участки двуслюдяных гранитов характеризуются проявлением площадной альбитизации полевых шпатов и мусковитизации биотита, а также пониженными по сравнению с неизменными гранитами, содержаниями олова. Мусковиты содержат значительно меньше олова, чем биотиты из тех же проб (Табл. 4). Но встречаются и другие участки двуслюдяных и мусковитовых гранитов, которые содержат олово в больших количествах, чем неизмененные граниты, главным образом, в форме рассеянного акцессорного касситерита. В этих участках мусковиты содержат олова значительно больше, чем его содержится в биотитах. Но здесь характер изменения гранита уже иной.

Изучение перераспределения олова в гранитах при их постмагматических гидротермальных изменениях приводит к выводу, что ведущая роль в обогащении гидротермальных растворов оловом, принадлежит автометасоматическим постмагматическим процессам, наряду с некоторым обогащением рудоносных растворов оловом в результате магматической дифференциации. Таким образом, по мнению автора, основным источником олова при образовании оловянных месторождений следует считать твердый раскристаллизованный гранит, обогащенный оловом, главным образом, в виде изоморфносвязанной формы в решетке биотита.

Генетическая связь оловорудных месторождений с "оловоносными гранитами" при такой трактовке вполне очевидна.

При поисках оловянных месторождений, основной вопрос — определение перспективности того или иного гранитного массива и его потенциальной возможности к формированию кварц-касситеритовых месторождений. Известно, что даже в пределах уже выявленных оловорудных провинций далеко не все интрузии гранитов оказываются рудоносными, а лишь некоторые из них, причем часто как те, так и другие внешне одинаковы. Поэтому, разработка методов быстрого определения "оловоносности" гранита имеет большое значение. "Оловоносным гранитом" следует называть такой гранит, который характеризуется признаками, указывающими на потенциальную возможность образования связанных с ним оловорудных месторождений, на его перспективность. Рассмотрение выделяемых в настоящее время петрохимических, минералогических и структурно-геологических признаков "оловоносных гранитов" показывает, что большинство из них являются недостаточными. Для определения "оловоносности" гранитных массивов следует рекомендовать прямой геохимический метод, основанный на знании распределения олова в "оловоносных" и "неоловоносных" гранитах, т.е. путем определения содержаний олова в неизмененных разностях гранитов, или, что быстрее и проще, его содержаний в биотитах. Выяснение же характера перераспределения олова при постмагматических изменениях гранитов, позволит более правильно и обоснованно выбрать дальнейшее направление поисковых работ.

При обследовании ряда оловянных месторождений кварц-касситеритовой формации на них было установлено наличие вертикальной зональности, которая выражается в смене характера околожильных изменений при прослеживании оруденения на глубину. Верхняя, рудоносная зона характеризуется развитием симметричных грейзеновых оторочек жил, которые при удалении от жилы, на коротком расстоянии переходят в неизмененные биотитовые граниты. В околожильных грейзенах встречаются касситерит, флюорит, топаз. С глубиной, мощность зон грейзеновых оторочек сокращается, тогда как ширина зоны альбитизации и мусковитизации вмещающих жилу гранитов увеличивается, причем разрастание зоны альбитизации с глубиной опережает разрастание мусковитизации. В нижней — подрудной зоне призальбандовой грейзенизации почти не наблюдается, а альбитизация и мусковитизация гранита приобретает площадной характер. В измененных гранитах подрудной зоны встречается турмалин, арсенопирит и апатит.

Химическая интерпретация описанной вертикальной зональности приводит к выводу о невозможности ее объяснения с точки зрения существующих гипотез о формах переноса олова в гидротермальных растворах (Бишоф, Джонс, Герценберг и Альфельд, Симонс, Стрелкин и др.), в том числе и с позиций наиболее распространенной гипотезы Добре.

По гипотезе Добре олово выносится из кристаллизующихся интрузивов в газовой фазе в виде SnF_4, которое, реагируя с водой в трещинах вмещающих пород, гидролизуется с образованием касситерита по реакции:

$$SnF_4 + 2H_2O \rightleftarrows SnO_2 + 4HF$$

или, как это предполагал Вагнер, по реакции:

$$SnF_4 + SiO_2 \rightleftarrows SnO_2 + SiF_4$$

Считается, что гипотеза Добре подтверждается следующими минералообразовательными процессами, сопровождающими выделение касситерита:

1. Разложением полевых шпатов плавиковой кислотой с образованием топаза и кварца,

2. Разложением полевых шпатов с образованием фторсодержащих слюд (мусковит, цинвальдит) и кварца,

3. Образованием флюорита.

Поскольку олово обладает ярко выраженными амфотерными свойствами и может находиться в виде катиона только в кислой среде, то и реакция Добре может иметь место только в условиях кислой среды. В то же время, такие минералы как кварц, фторсодержащий мусковит и флюорит были искусственно получены из щелочных растворов (Вульчин, Ноль, Сенармон, Машне и др). Это говорит за то, что фторсодержащие минералы, сопровождающие касситерит, могут образовываться не только из кислой среды. Более того, наблюдаемые на кварц-касситеритовых месторождениях случаи перехода кальцитовых прожилков во флюоритовые, наличие выделений гипогенного кальцита по спайности мусковита и в самих кварцевых жилах, а также повсеместно отмечаемая тесная связь процесса образования коренных оловянных месторождений с процессами альбитизации полевых шпатов и мусковитизации биотита гранитоидов, которые во времени предшествуют образованию оловоносных жил, — однозначно указывает на щелочной характер рудоносных растворов.

В этих условиях SnF_4 существовать не может.

Из химии олова известно, что одним из очень характерных свойств галогенида SnF_4, является его сильно выраженная склонность к реакциям присоединения фторча х щелозей, с образованием солей галогеноводородной комплексной кислоты типа $Na_2\ [SnF_6]$. С другой стороны, еще Беллучи и Паравано (1904), показали, что станнат натрия следует рассматривать как натровую соль комплексной гексаоксикислоты типа $Na_2[Sn(OH)_6]$.

Интересно также упомянуть об опытах Тронева В. Г. и Хреновой А. Л. (1946), которые при температуре 300° и давлении 90-100 атм. добились стопроцентного перевода касситерита в щелочной раствор. Анализ кристаллов, осажденных после растворения SnO_2 в растворе NaOH близко отвечал соединению $Na_2[Sn(OH)_6]$. С другой стороны, Смит Ф. Г. (1947) экспериментально показал, что касситерит кристаллизуется из раствора станната натрия при уменьшении его щелочности за счет связывания натрия кварцем, с образованием силиката натрия.

Оба комплексные соединения олова хорошо растворимы и устойчивы в щелочных водных растворах.

Но, как известно, ионы фтора и гидроксила, обладая одинаковым зарядом и очень близкими ионными радиусами, взаимозаменяемы в своих соединениях. Поэтому, в природных водных растворах, содержащих фтор, трудно предполагать существование чистого соединения Na_2SnF_6. Скорее всего, в этих растворах будет образовываться какое-то промежуточное соединение типа $Na_2[Sn(OH, F)_6]$. При подкислении щелочного раствора $Na_2[Sn(OH)_6]$, гидролиз наступает при pH = 7. При подкислении щелочного раствора Na_2SnF_6 гидролиз наступает при различных значениях pH от 7 до 8, в зависимости от степени разбавления раствора. Чем более разбавлен раствор, тем ближе к pH = 7 наступает гидролиз, что, повидимому, связано с возрастающей ролью гидроксила в комплексном анионе по мере разбавления раствора.

Поскольку природные гидротермальные растворы вероятнее всего являются достаточно разбавленными, то гидролиз соединения предположительно будет происходить в интервале pH от 7 до 7,5, т.е. в нейтральной или скорее в слабощелочной среде.

Как показал Томсен (1906) при гидролизе соединение Na_2SnF_6 распадается на гидрат оловянной кислоты, плавиковую кислоту и фтористый натрий. Энгель выяснил, что гидрат оловянной кислоты последующими коллоиднохимическими процессами может переводиться во все более бедные водой формы, вплоть до получения двуокиси олова. Этому, повидимому, будет способствовать также увеличение кислотности среды.

Таким образом распад наиболее вероятного в природных условиях соединения $Na_2[Sn(OH,F)_6]$ можно представить следующим образом:

$$\begin{aligned}
Na_2[Sn(OH,F)_6] + 2H_2O &\rightleftharpoons Sn(OH)_4 + 2NaF + 2HF \\
Sn(OH)_4 &\rightleftharpoons SnO(OH)_2 + H_2O \\
SnO(OH)_2 &\rightleftharpoons SnO_2 + 2H_2O \\
\hline
Na_2[Sn(OH,F)_6] &\rightleftharpoons SnO_2 + 2NaF + 2HF
\end{aligned}$$

Выделяющаяся при этом плавиковая кислота и будет вызывать разложение полевых шпатов с образованием топаза, мусковита, флюорита и кварца. Другими словами, пойдут как раз те минералообразовательные процессы, которыми обычно подтверждают гипотезу Добре, что лишний раз показывает всю необоснованность этих "доказательств".

Но поскольку в рудоносных растворах кроме олова находится большое число других ионов, часть из которых также образует комплексные фтористые соединения, то необходимо рассмотрети возможные случаи конкуренции с оловом этих ионов.

Кремний образует кремнефтористый комплекс $[SiF_6]^{-2}$, но его константа нестойкости $K = 7 \cdot 10^{-7}$ (Рысс Г. И., 1946) очень велика, что говорит о его малой прочности. Кроме того, фторсиликат натрия плохо растворим в воде и разлагается под действием щелочей (даже аммиаком). Следовательно, крамний не может конкурировать с оловом, образующим фтористооловянный комплекс. Константа нестойкости $[AlF_6]^{-3}$ $K = 2 \cdot 10^{-24}$, наоборот, очень мала, и прочность этого комплекса достаточно велика. Но, поскольку алюминий хорошо растворим только в сильно щелочных и сильно кислых растворах, и очень мало растворим в нейтральных, в слабощелочных рудоносных растворах его миграция будет весьма ограниченна и присутствие его в растворе не будет сколько-либо существенно сказываться на поведении фтористо-оловянного комплекса.

Также затруднительно в этих условиях и перемещение магния.

Более сложная картина наблюдается с кальцием, более или менее постоянно присутствующим в рудоносном растворе. Однако, до начала распада фтористооловянного комплекса, он также не связывается с фтором и поэтому не влияет на поведение комплекса $[Sn(OH,F_6)]^{-2}$ т.к. в рудоносном растворе имеется ион $(PO_4)^{-3}$, а произведение растворимости у $Ca_3\,(PO_4)_2$ — $1 \cdot 10^{-25}$ значительно меньше, чем у CaF_2 — $3{,}4 \cdot 10^{-11}$, тогда как теплота образования наоборот — существенно больше (соответственно 983 и 290 $\frac{\text{К - кал}}{\text{г. моль}}$). Поэтому, до усреднения раствора, в щелочной среде кальций будет связываться с ионом $(PO_4)^{-3}$, образуя апатит, и только после усреднения раствора, когда затрудняется миграция фосфора и начинается распад оловяннофтористого комплекса, кальций связывается с фтором, образуя флюорит.

Все изложенное выше, позволяет нам высказать предположение о переносе олова гидротермальными растворами в виде соединения $Na_2[Sn(OH,F)_6]$.

Возникновение описанной вертикальной зональности на кварц-касситеритовых месторождениях с позиций предлагаемой нами гипотезы о формах переноса олова гидротермальными растворами — вполне закономерна. Действительно, если щелочные (существенно натровые) гидротермальные растворы поднимаются по ослабленным участкам, по открытым трещинам и зонам дробление в гранитах, то они будут вызывать альбитизацию полевых шпатов и, как следствие этого, мусковитизацию биотита. Вытесняемое при этом из кристаллической решетки биотита олово будет поступать в гидротермальный раствор, образовывать фтор-гидроксильный комплекс и мигрировать с раствором в вышележащие горизонты.

Но по мере связывания натрия, щелочность растворов будет уменьшаться и приближаться к щелочности порового раствора гранита, т.е. они будут становиться слабощелочными, близкими к нейтральным. В этих условиях, близких к достижению равновесия между рудоносным и поровым раствором гранита начинается гидролиз комплексного соединения, несущего олово и выпадение касситерита. При распаде соединения $Na_2[Sn(OH,F)_6]$ выделяется свободная фтористоводородная кислота, что вызывает быстрое подкисление рудоносного раствора, который становится более кислым, чем поровый раствор гранита.

В результате, привнос натрия во вмещающие рудопроводящий канал породы сменяется выносом щелочей из вмещающих пород, что минералогически выражается в грейзенизации гранита и образовании мусковитовых оторочек жил. Другими словами, возникает как раз описанная выше вертикальная зональность. Исходя из изложенной схемы химизма рудообразования, в корнях кварц-кассетиритовых жил должны существовать зоны интенсивного выноса олова из околожильных гранитов, а в верхней рудоносной части жилы, наоборот — привнос олова во вмещающие жилу грейзенизированные граниты.

Следовательно, вертикальная зональность на кварц-касситеритовых месторождениях должна выражаться не только в различии характера околожильных изменений, но и в различном характере распределения олова в околожильных гранитах.

Действительно, изучение распределения олова в околожильных гранитах, на целом ряде месторождений показало, что характер этого распределения закономерно изменяется при прослеживании оруденения на глубину, в соответствии с установленной по околожильным изменениям вертикальной зональностью.

Верхняя рудоносная зона характеризуется планомерным переходом при удалении от жилы (вкрест ее простирания) от резко повышенных содержаний в призальбандовом грейзене до нормального содержания олова в неизмененных гранитах. При приближении нижней подрудной зоны, на значительном протяжении по простиранию жилы начинает намечаться вынос олова из призальбандовых гранитов, но зона выноса имеет еще незначительную мощность.

На вскрытие же нижней подрудной зоны, наряду со сменой характера околожильных изменений, указывает и появление зоны интенсивного выноса олова из вмещающих пород, значительной мощности.

Но выяснение характера распределения олова в околожильных гранитах позволяет не только производить оценду продолжения оруденения на глубину,но и позволяет предвидеть распределение полезного компонента на следующем ниже, еще не вскрытом горизонте. Например, другая жила того же месторождения до 3-го горизонта обнаруживала высокие, в несколько раз превышающие кондиционные, содержания Sn. На 3-м горизонте содержания Sn снизились почти до кондиционных.

Из рассмотрения этих данных видно, что в центральной части намечается зона выноса. Sn из вмещающих гранитов, но на значительно большем протяжении, в обоих фланговых частях отмечаются все характерные черты верхней рудоносной зоны, причем южный фланг отвечает более высоким горизонтам этой зоны, чем северный. На основании этого было сделано предположение, что падение содержания Sn на 3-м горизонте является случайным, обусловленным общим неравномерным распределением дасситерита по жиле. Промышленное оруденение должно продолжаться ниже, на протяжении одного-двух горизонтов, и на 4-м горизонте следует ждать увеличения содержания Sn. Причем, на южном фланге содержание Sn будет выше, чем на северном, а в центре — меньше, нем на флангах. Опробование пройденных на 4-м горизонте штреков по этой жиле подтвердило правильность сделанного предположения.

Таким образом, выяснение распределения и перераспределения олова в гранитах, а также изучение минералогического характера изменений и распределения олова в околожильных гранитах позволяет с совершенно новых геохимических позиций подойти к решению вопросов генетической связи оруденения с интрузиями, к пониманию условий формирования оловорудных месторождений. А использование геохимических поисковых и оценочных критериев в геолого-разведочной службе, поможет геологам более обоснованно и более эффективно проводить поиски и оценку кварц-касситеритовых месторождений.

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DISTRIBUTION PRIMAIRE DE Li, Be, Sn DANS LES MINÉRAUX COMMUNS DES GRANITES. APLICATIONS À LA PROSPECTION GÉOCHIMIQUE

J. JEDWAB *

RESUME

Les halos de dispersion primaires sont actuellement très peu utilisés dans la prospection géochimique. Il existe cependant des régularités dans la distribution des traces d'éléments contenus dans les minéraux communs des roches magmatiques, qui permettent d'aborder un des problèmes fondamentaux de la prospection géochimique, le pronostic précoce de la minéralisation d'un massif pétrographique. L'étude de la distribution de Li Be Sn dans quelques granites montre que l'on peut assez aisément distinguer les granites auxquels sont génétiquement des gisements de ces éléments.

INTRODUCTION

La recherche rationnelle des gisements minéraux primaires ou des districts minéralisés par l'étude des halos de dispersion primaire des éléments n'est pas encore entrée dans la pratique de la prospection géochimique. L'intérêt que les prospecteurs manifestent depuis una dizaine d'années pour les méthodes géochimiques se porte exclusivement sur les halos secondaires, dont le rendement est plus inmmédiat. Il n'est cependant pas prématuré d'aborder la question des dispersions primaires: pour résoudre les problèmes que posent par exemple les granites et leurs minéralisations, la connaissance des distributions spaciales et minéralogiques des traces d'éléments serait, pensons-nous, d'un très grand secours théorique et pratique. Citons parmi ces problèmes: le pronostic et la localisation des minéralisations, la corrélation de granites spacialement éloignés, la distinction de granites contigus et de granites d'origines différentes. Nous nous occuperons plus particulièrement ici du pronostic de minéralisation dans les granites.

Il existe dans la littérature de rares indications sur les relations positives qui existent entre les teneurs en traces d'éléments dans les granites (et leurs

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minéraux) et la présence de minéralisation; nous en avions déjà dressé une liste incomplète (Jedwab 1955). Dans une série de travaux spectrochimiques portant sur des granites choisis en fonction de la présence ou de l'absence de minéralisation en Li, Be ou Sn, nous avons pu mettre en évidence une série de régularités intéressantes. Nous devons attirer l'attention sur le fait que ces régularités sont présentées comme des indications pour les recherches futures, et non comme des lois générales achevées.

Le tableau I groupe des indications géologiques et bibliographiques concernant les granites que nous avons analysés.

Nous pouvons répartir ces granites de la manière suivante:

I—Granites non minéralisés en Li, Be ou Sn: Guéhenno, Egletons, Montebras (gran. à biot.) Bénévent, Nantuat, Schwarzwald.
II—Granites minéralisés en Li, Sn mais pas en Be: Maymac, Carnmenellis Baveno.
III—Granites minéralisés en Li, Be mais pas ou peu en Sn: Bessines, I. d'Elbe.
IV—Granites à minéralisation complexe: La Villeder, Montebras.

DÉTAILS ANALYTIQUES

Chaque échantillon de granite a été constitué de 4 à 6 fragments de 30-50 gr prélevès dans un rayon de 5 à 10 m dans la mesure du possible. Ces échantillons ont été broyés à la presse hydraulique, et les minéraux séparés sous la loupe binoculaire avec la pince. Les feldspaths n'ont pas été différenciés. Les minéraux ont été écrasés entre tas de verre, revérifiés pour leur pureté, et mélangés avec un poids égal de carbone spetrographique dans le mortier d'agate. Ils ont été analysés par spectrographie optique d'émission avec un spectrographe Hilger (Large), suivant une méthode semi-quantitative combinant les méthodes de Mannkopf et de Harvey.

Raies utilisées: Li 3232 Be: 2348 Sn: 3175

Limites de sensibilité:	Biotites:			Feldspaths:		
		Li	30 ppm		Li	300 ppm
		Be	3 ppm		Be	3 ppm
		Sn	10 ppm			

Les résultats des analyses spectrochimiques ont été rassemblés dans le tableau II. Leur comparaison permet de faire quelques remarques, qui peuvent servir de conclusions et d'hypothèses de travail provisoires. Elles sont d'autant plus marquées et valables que l'on choisit comme termes de comparaison des granites différemment minéralisés et voisins.

Nous pensons pouvoir tirer les conclusions suivantes de ces analyses:

1—Les granites non minéralisés en Li Be ou Sn ont des biotites très pauvres en Li Be Sn: Egletons, Bénévent, Nantuat, Schwarzwald.

TABLEAU I

GRANITES ETUDIÉS

Pays	Localité	Orogénèse	Caractère de la roche	Minéralisations associées	Sources bibliographiques
France	La Villeder	Varisque	Gr. à 2 micas	Filons de quarts à Sn Be-As	Tronquoy (1912)
	Guéhenno	id	id	Pegm. à tourmaline.	Jedwah (1955a)
	Montebras	id	id	Pegm. à Sn Nb Ta Li Be W	Lacroix (1893-1913)
	Montebras	id	Gr. à biotite	Non minéralisé.	
	Bessines	id	Gr. à 2 micas	Pegm. à Be (zone minéralisée)	Lacroix (1893-1913)
	Bessines (rég. de)	id	id	Pegm. communes (zone non minéralisée)	Jedwab (1956)
	Bénévent-l'Abbaye	id	Gr. à biotite	Pas de minéralisation	
	Nantiat	id	id	id	id
	Egletins	id(?)	Gr. à biotite	Pegm. à grenats.	Rondot (1948)
	Meymac	id	Gr. à 2 micas	Filons de quartz à Sn W	
Grande Bretagne	Carnmenellis	id	Gr. à 2 micas	Filons de quartz à Sn, Cu, etc. Pegm. à Bertrandit, tourm.	Ghosh (1943) Dewey (1948) Hosking (1952)
Italie	Baveno	(?)	Gr. à 2 micas	Druses à oligiste, zéol., zinnwaldite, etc. Pas de Be.	
	I. d'Elbe	Alpine	Gr. à 2 micas	Pegm. à Be B Cs Li Sn	Ferslan (1909)
Allemagne	Malzburg	Varisque	Gr. à biotite	Pas de minéralitation Li Sn Be	Schneiderhön (1941)
	St Blasien	id	id	id	
	Schluchsee	id	id	id	
	Triberg	id	id	id	
	Blauen	id	id	id	

TABLEAU II

RÉSULTATS DES ANALYSES SPECTROCHIMIQUES

LOCALITÉ	NOMBRE D' ÉCHANTILLONS	CONCENTRATION MOYENE DANS LES BIOTITES EN PPM			CONCENTRATION MOYENE DANS LES FELDSPATHS EN PPM	
		Li	Sn	Be	Li	Be
La Villeder	Biit.: 25 Feldsp.: 30	n.d.	110	n.d.	141	n.d.
Guéhenno	Biot.. 10 Feldsp.: 11	n.d.	77	n.d.	36	n.d.
Montebras	Gr. à 2 micas: 5	3654	404	17	354	17
	Gr. à Biot.: 5	380	201	16	246	17
Bessines	Zone min. en Be: 16	970	205	12,5	n.d.	42
	Zone non min. en Be: 19	330	202	33,8	n.d.	14,5
Bénévent-Nantiat	4	121	0	0	n.d.	0
Egletins	1	165	25	0	n.d.	0
Meymac	1	540	33	11	n.d.	11
Carnmenellis	9	853	131	28	tr	0
Baveno	2	765	135	28	0	0
I. d'Elbe	4	645	39	10,7	tr	31,5
Malzburg	3	95	83	n.d.	n.d.	n.d.
St Blasien	1	68	37	n.d.	n.d.	n.d.
Schluchsee	1	210	42	n.d.	n.d.	n.d.
Triberg	2	135	94	n.d.	n.d.	n.d.
Blauen	1	110	48	n.d.	n.d.	n.d.
Moyenne Schwarzwald	8	77	38			

2—Les granites minéralisés en Li, Sn (ou l'un des deux) mais pas en Be ont des biotites riches en Be et des feldspaths pauvres en ou dépourvus de Be: Carnmenellis, Baveno, Bessines (zone non minéralisée).

3—Les granites minéralisés en Be ont des feldspaths riches en Be: Bessines (zone minéralisée), I. d'Elbe.

4—Les granites minéralisés en Li ont des biotites riches en Li: Montebras, Bessines, Carnmenellis, I. d'Elbe, Baveno.

5—Les granites minéralisés en Sn ont des biotites riches en Sn: La Villeder, Montebras, Carnmenellis.

6—Le Li dans les feldspaths présente dans certains cas une relation avec la minéralisation: La Villeder.

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К ГЕОХИМИИ Pb И Zn В ГРАНИТОИДАХ

Л. В. Таусон *

ABSTRACT

The study of lead and zinc geochemistry in the Caledonian granite complex of the Central Tian-Shan has shown that in the course of the differentiation of the magma an accumulation of lead in acid differentiated, and an impoverishment of the latter by zinc, occurred. The zinc-lead ratio changes from 10 in diorites of the first intrusion phase to 0.5 in gangue granite-aplites.

The examination of the lead distribution in the minerals of granitoids has shown that about 80 percent of this element is restricted to feldspars. In potassium feldspars they are almost always found in the form of an isomorphous impurity. About 40 percent of the rock lead is contained in an "extra silicate" form which may be easily leached out and which mineralogically is largely represented by submicroscopic galena or native lead isolations.

About 70 percent of the zinc contained in the granitoids is concentrated in the iron-magnesium silicates. The zinc content of these minerals exceeds by more than tenfold the general content of the elements in the rock; however, almost all the zinc is not contained in this mineral in the form of an isomorphous impurity and over 80 percent of it is extracted from the rock by specific solvents. It is assumed that most of the zinc atoms are contained in the rocks in a mobile "extra silicate" form.

The peculiarities of the lead and zinc distribution in granitoids and the high migration capability of these elements stipulate a considerable shift of the ore substance even during low temperature postmagmatic processes. A study of the altered granitoid varieties shows the important role of primary dissemination patterns which may become an important criterion in prospecting work.

Изучение геохимии редких и рудных элементов в изверженных горных породах в настоящее время является одной из актуальных проблем геохимии. Общие теоретические основы этой проблемы били сформулированы основоположниками геохимии В. И. Вернадским и В. М. Гольдшмидтом еще в начале нашего столетия. Однако, если на заре геохимии эта проблема рассматривалась как важная, но в основном теоретическая область геохимии, то в настоящее время она становится одним из обещающих путей к ре-

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шению основной задачи геологии — выявлению закономерностей в концентрации рудного вещества. Учитывая подобную направленность изучаемой проблемы, представляется, что исследования в области геохимии редких и рудных элементов в изверженных горных породах должны в основном осветить три вопроса:

1. Геохимическая история элементов в ходе развития магматического очага и металлогеническая специализация магм.

2. Распределение элементов по минералам пород и формы их нахождения в породах.

3. Миграция элементов при постмагматических процессах изменения пород.

В настоящей работе рассматриваются, в основном, вопросы геохимической истории свинца и цинка в ходе развития крупного магматического очага, а также распределение этих элементов по минералам пород и формы их нахождения в породах.

Применительно к свинцу и цинку, некоторые данные об их геохимической истории в ходе дифференциации магмы могут быть заимствованы из работ, в которых приводятся сведения о содержании этих элементов в основных типах изверженных пород. Все эти исследования указывают на накопление Pb в кислых изверженных породах и Zn в основных. Изучение геохимии этих элементов в каледонских гранитоидах Сусамырского батолита (Центр. Тяньшань) позволяет выявить некоторые особенности геохимической истории Pb и Zn в ходе развития единого, весьма крупного магматического очага.

Сусамырский батолит (в описываемой его части) занимает площадь в 7,500 км^2. Главный интрузивный каледонский комплекс представлен тремя фазами, последовательно внедрившимися в толщи протерозоя и нижнего палеозоя. К первой, наиболее ранней фазе внедрения относятся диориты и габбродиориты, образующие небольшие по площади штоки во вмещающих породах или крупные ксенолиты в более молодых интрузивных породах. Наибольшим распространением пользуются порфировидные граниты и гранодиориты второй фазы внедрения, которые местами переходят в тоналиты, кварцевые диориты и адамелиты. Третья фаза внедрения представлена среднезернистыми лейкократовыми гранитами. Жильная серия комплекса представлена гранитами, гранит-порфирами и аплитами. Кроме пород, относящихся к описанному выше основному каледонскому комплексу, в районе, на сравнительно ограниченной площади обнажаются крупнозернистые биотитовые граниты. Возрастные взаимоотношения интрузии биотитовых гранитов с породами основного каледонского комплекса пока неясны. Изучение распределения Pb и Zn в неизмененных разностях основных фаз внедрения каледонского комплекса, предпринятое на обширном каменном материале, предварительно описанном петрографически, показало совершенно определенную склонность свинца к накоплению в более кислых, а цинка в более основных дифференциатах гранитного комплекса.

Как видно на табл. 1, эти особенности геохимической истории свинца и цинка особенно отчетливо проявляются, с одной стороны, в крайных членах комплекса, а с другой в изменении отношения Zn/Pb от 10,7 для диоритов и габбродиоритов до 0,3 для жильных аплитов.

Полученные результаты дают возможность рассчитать средние содержания свинца и цинка для интрузий Сусамырского батолита. Принимая, что порфировидные граниты (γ_1^2) занимают около 80% всей площади обнажающихся изверженных пород, а лейкократовые граниты (γ_1^3) и биотитовые граниты ($_2$?) только но 10% площади, среднее содержание свинца для гранитоидов района может быть принято в $2{,}5 \cdot 10^{-3}$%, а среднее содержание цинка $5{,}4 \cdot 10^{-3}$%. Как видно, полученная цифра по свинцу существенно выше той, которая принимается в качестве кларка для литосферы ($1{,}5 \cdot 10^{-3}$%),* в то время как для цинка полученная цифра хорошо согласуется с кларками этого элемента в литосфере ($5{,}0 \cdot 10^{-3}$%).

Анализ полученных результатов по содержанию свинца и цинка в породах наиболее распространенной второй фазы внедрения (порфировидных гранитах) дает возможность сделать ряд замечаний, касающихся более частных вопросов.

На рис. 1 видно, что для основной массы проанализированных образцов пород этой фазы внедрения содержание Pb колеблется в пределах 20-30 γ/г. Таким образом, в случае пород одной и той же фазы внедрения, несмотря на петрографические различия отдельных фаций (от тоналитов до гранитов), содержание свинца в них колеблется незначительно (рис. 1).

В случае цинка наблюдается совершенно иная картина. Как видно на рис. 2, содержание Zn в породах этой же фазы внедрения колеблются весьма значительно — от 30 до 96 γ/г породы. При этом, только в случае очень высоких содержаний цинка (от 80 до 95 γ/г породых) проявляется некоторая приуроченность их к меланократовым разностям пород (рис. 2).

В интервале же от 40 до 70 γ, на который приходится более 3/4 проанализированных образцов, какой-либо связи между содержанием цинка и петрографическими особенностями пород пока не установлено. Необходимо заметить, что подобные же колебания в содержаниях цинка отмечались и другими исследователями. Так, Е. В. Сендел и С. С. Голдич

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* Кларковое содержание Pb принимается равным $1{,}5 \cdot 10^{-3}$% и Zn $5 \cdot 10^{-3}$% (А. П. Виноградов, 1955).

Таблица 1

Распределение Pb и Zn в основных фазах внедрения гранитоидов Сусамырского батолита

Основные фазы внедрения	Содержание		Отношение
	Pb	Zn	Zn/Pb
	(в γ/г)		
Диориты и габбродиориты (сред. из анализа 10 образцов)	9	97	10,7
Порфировидные граниты и гранодиориты (γ_1^2) (средн. из анализа 74 образцов)	25	56	2,2
Лейкократовые граниты (γ_1^3) (средн. из анализа 18 образцов)	31	29	0,9
Жильные породы (только аплиты) (средн. из анализа 7 образцов)	39	10	0,3
Крупнозернистые биотитовые граниты (γ_2?) средн. из анализа 15 образцов)	22	65	2,9

(1952), при анализах гранитных пород из округа Льяно (Ц. Техас) установили колебание в содержаниях цинка от 40 до 120 γ. Содержание Zn в европейских гранитах, приводимое С. Х. Веденолем (1953), колеблется от 5 до 85 γ. Наконец, Иошими Морита (1955), приводя анализы на Cu и Zn для различных типов пород, указывает, что в случае гранитов содержание Zn колеблется от 10 до 75 γ/г породы.

Вместе с тем, сопоставление содержаний Pb и Zn в порфировидных гранитах γ_1^2 для отдельных районов батолита показывает наличие некоторых различий для отдельных его частей (табл. 2).

Таблица 2

Район	Количество образцов	Положение в батолите	Содержание (в γ/г)		Отношение Zn/Pb
			Pb	Zn	
Хр. Джумгол (центр. и вост. часть)	16	Восточная часть батолита	19	60	3,1
Хр. С. Кавак-Тау	14	Центр. часть батолита	25	61	2,4
Хр. Джумгол (западн. часть)	19	” ”	26	56	2,2
Хр. Сарыкамыш	10	” ”	28	57	2,0
Хр. Сусамыр (восточн. часть)	15	Западная часть батолита	26	44	1,7
Среднее для гранитоидов γ_1^2	74		25	56	2,2

Как видно, в восточной части батолита распространены породы, отличающиеся низким содержанием свинца. В центральной части батолита содержание свинца и цинка оказывается весьма близким к среднему значению содержания этих элементов в гранитоидах данной фазы внедрения. Наконец, в породах западной части батолита наблюдается относительное уменьшение содержания цинка.

При этом необходимо заметить, что как в западной, так и в восточной частях батолита вмещающие породы относятся к нижнему палеозою, в то время как в центральной части батолита среди вмещающих пород существенную роль играют метаморфические толщи протерозоя. Сопоставление всех этих фактов дает основание предполагать, что в случае Pb и Zn, металлогеническая специализация интрузий не определяется решающим влиянием вмещающих пород верхнего структурного яруса, как предполагают некоторые исследователи (Абдуллаев, X. М., 1954). Вероятнее всего, основными факторами, определяющими металлогеническую специфику гранитных интрузий в отношении Pb и Zn в районе Сусамырского батолита являются содержание этих элементов в первичной магме и особенности глубинной ассимиляции вмещающих пород.

Для последующих членов описываемого магматического комплекса территориальные различия в содержаниях Pb и Zn уже почти не проявляются и колебания в содержании цинка несколько меньше. В лейкократовых гранитах γ_1^3 содержание Pb колеблется от 24 до 40 γ; Zn — от 20 до 40 γ. В жильных аплитах содержание свинца колеблется от 26 до 48 γ и цинка — от 8 до 16 γ.

Таким образом, изучение характера распределения Pb и Zn в породах Сусамырского каледонского гранитного комплекса дает основание сделать два основных вывода:

1) В ходе развития магматического очага свинец стремится накапливаться в кислых дифференциатах, в то время как содержание цинка в этих более поздних членах магматического комплекса падает.

2) Содержание Pb и Zn в главных фазах внедрения определяется в основном содержанием этих элементов в первичной магме, глубинной ассимиляцией вмещающих пород при становлении интрузии, и последующим ходом дифференциации образовавшегося магматического очага.

Как уже указывалось, вторым важнейшим вопросом геохимии редких и рудных элементов в изверженных горных породах являются формы нахождения и первичное распределение элементов по минералам пород. Формы нахождения и характер первичного распределения рудных элементов в породах находится в связи с вопросами потенциальной рудоносности интрузий и миграции этих элементов при постмагматических процессах изменения пород.

Существующие до сих пор представления о формах нахождения и характере распределения Pb и Zn по минералам изверженных пород несколько противоречивы.

С одной стороны, вследствие близости ионных радиусов свинца и калия (Pb^{2+} — 1,32 Å; K^{+} — 1,33 Å) предполагается возможность изоморфного вхождения свинца в калиевые минералы. С другой стороны, ряд исследователей признает возможность нахождения Pb в породах в виде галенита.

Изучение распределения свинца по минералам основных петрографических разностей каледонских гранитоидов Сусамырского батолита пока-

Таблица 3

Распределение свинца по минералам каледонских гранитов Сусамырского батолита

Минерал	Содержание минерала в породе (в вес.%)	Содержание Pb в минерале (в γ/г)	Колич. в минерале при пересчете на 1 г породы (в γ)	% Pb породы, приходящ. на данный минерал	Общее содержание Pb в породе (в γ/г)
Неравномернозернистый гранит γ_1^2					
Кварц	35,0	4	1,4	5,4	
Плагиоклазы	27,6	40	11,0	42,3	
К-полевые шпаты	32,7	40	13,1	50,4	
Биотит	4,0	20	0,8	3,1	
Магнетит	0,6	17	0,1	0,4	
Сумма			26,4	101,6	26
Крупнозернистый биотит — роговообманковый гранит γ^2 ?					
Кварц	30,0	2	0,6	3	
Плагиоклазы	24,0	26	6,2	3,1	
К-полевые шпаты	41,0	30	12,5	61,5	
Биотит	4,2	14	0,6	3	
Роговая обманка	0,75	8	0,1	0,5	
Магнетит	0,35	6	—	—	
Сумма			19,8	99,0	20
Лейкократовый среднезернистый гранит γ_1^3					
Кварц	32,0	3	1	3,3	
Полевые шпаты	65,0	35	22,8	76,0	
Биотит	3,4	20	0,7	2,3	
Магнетит	0,35	20	0,1	0,3	
Сумма			24,6	81,9	30

зало, что основная масса этого элемента сконцентрирована в полевых шпатах пород (табл. 3).

Как видно из табл. 3, на долю полевых шпатов приходится от 76 до 93% свинца пород. При этом обращает внимание тот факт, что содержание этого элемента в К-полевых шпатах не отличается от его содержания в плагиоклазах. Если в К-полевых шпатах можно предполагать изоморфное вхождение свинца, то в случае плагиоклазов это явно затруднительно, так как никаких данных о возможности замещения свинцом натрия или кальция нет. Обращает на себя внимание и тот факт, что в другом калиевом минерале-биотите содержание свинца по всех случаях в два раза меньше, нежели в полевых шпатах и мало отличается от содержания явно не изоморфного свинца в магнетите. Подобное различие в содержаниях свинца в двух калиевых минералах, видимо, объясняется структурным положением калия. Как известно, калий в биотите имеет очень большое координационное число. Вместе с тем известно и то, что структуры с ковалентными связями часто характеризуются низкими координационными числами. Возможно, что существенно ковалентный характер связи свинца с кислородом и обусловливает то, что он легче замещает калий в тех силикатных структурах, в которых этот элемент имеет менчшее координационное число, — т.е. в К-полевых шпатах.

Характер распределения свинца по минералам пород дал основание предположить, что только некоторая часть свинца породы будет изоморфно связана в калиевых минералах. Другая же часть свинца породы, видимо, будет находиться в виде так называемой "внесиликатной" формы, минералогически представленной, вероятно, субмикроскопическими выделениями преимущественно галенита или самородного свинца.

Для проверки этого предположения было проведено избирательное выщелачивание свинца из породы. В качестве реагента была взята 0,2 N соляная кислота с добавкой NaCl из расчета 1 г/литр раствора. Кислота подобной концентрации почти не разрушает силикатов, но хорошо растворяет природный галенит и сфалерит. Добавление в реагент NaCl обусловлено тем, что в избытке хлористого натрия будет образовываться комплекс типа $Na_2[Pb\ Cl_4]$, с большей растворимостью, нежели у $PbCl_2$. Результаты опытов по выщелачиванию сведены в табл. 4.

Как видно, в результате подобного избирательного выщелачивания, из пороы извлекается от 30 до 50% находящегося в ней свинца.

Ряд образцов был подвергнут четырехкратному выщелачиванию, причем выход Pb определялся после каждого выщелачивания. Эти опыты показали, что основная масса выщелачиваемого свинца мобилизуется из породы уже при первом выщелачивании (75-80% от всего извлекаемого свинца)

Таблица 4

Выщелачивание из некоторых каледонских гранитоидов

Таблица 4

Выщелачивание из некоторых каледонских гранитоидов Сусамырского батолита

Образец	Общее содержание Pb в породе (в γ /г)	Количество Pb извлеченного из породы в результате 2-х выщелачив. (в γ /г)	Количество Pb в остатке после выщелачивания (в γ /г)	Сумма выщелоченного и оставшегося Pb (в γ /г породы)	% выщелачивания	Примечание
Порфировидный гранит γ_1^2 (хр. Кавак-Тау)	20	9	12,5	21,5	42	% выщелачивания взят от суммы выщелоченного и оставшегося в породе свинца.
Меланократовый адамеллит γ_1^2 (хр. Сарыкамыш)	30	16,5	16	32,5	51	,, ,,
Тоналит γ_1^2 (хр. Джумгол)	20	7,5	12,5	20	37	,, ,,
Гранит γ_1^2 (хр. Сарыкамыш)	28	7,5	20	27,5	27	% выщелачивания взят от общего содержания Pb в породе
Гранит γ_1^2 (хр. Джумгол)	14	6	11	12	35	
Гранит γ_1^2 (хр. Джумгол)	26	8	13	21	31	,, ,,
Биотитовый гранит γ_1^2 (хр. Сусамыр)	22	10	10	20	45	,, ,,
Лейкократовый гранит γ_1^3 (хр. Джумгол)	30	10	18	28	33	,, ,,

и отчасти при втором. Третье и четвертое выщелачивания существенного выхода свинца в раствор не дают. Это дает основание предполагать, что при подобном выщелачивании переходящий в раствор свинец принадлежит каким-то легко растворимым в данной среде минералам. В частности, такими минералами могут быть галенит, самородный свинец и др. Выщелачивание свинца из фракций К-полевых шпатов некоторых гранитоидов показало, что в этом минерале почти весь свинец, видимо, является изоморфным (в среднем из К-полевых шпатов извлекалось 15% находящегося там свинца).

Таким образом, если в К-полевых шпатах изучавшихся гранитоидов свинец почти полностью находится в виде изоморфной примеси, то в других минералах породы он повидимому находится преимущественно в виде "внесиликатной" формы и легко выщелачивается специфическими растворителями. В связи с тем, что представление о "внесиликатной" форме свинца пока основывается только на наличии в породах химически доказанной легкоподвижной части атомов этого элемента говорить о минералогическом характере выделений этой формы очень трудно. При изучении протолочек описываемых гранитоидов в нескольких шлихах было отмечено наличие самородного свинца или галенита. На находки единичных зерен галенита и самородного свинца в гранитоидах указывали и другие исследователи (Туровский, С. Д., 1953). Можно предполагать, что минералогически "внесиликатная" форма свинца видимо будет представлена микроскопическим и субмикроскопическим выделениями свинцовых минералов (преимущественно галенита и самородного свинца), которые будут располагаться в интерстициях и по трещинам в породообразующих минералах.

Представления о распределении цинка по минералам пород также как и для свинца являются несколько противоречивыми. В. М. Гольдшмидт, а вслед за ним и многие другие исследователи считали, что цинк преимущественно должен концентрироваться в железо-магниевых силикатах, где он может легко замещать магний и двухвалентное железо (Zn^{2+} — 0,83 Å; Mg^{2+} — 0,78 Å и Fe^{2+} — 0,83 Å). Только Г. Нейманн (1944) предположил, что цинк в изверженных горных породах может находиться в виде субмикроскопических выделений сфалерита. Это предположение Нейманн обосновывал тем, что во всех собственных силикатных минералах цинк имеет четвертую координацию, вто время как в железомагниевых силикатах Fe^{2+} и Mg^{2+} имеют шестерную координацию. Это, по его мнению, должно затруднять возможность изоморфного вхождения цинка в данные минералы. Способность цинка входить в собственные силикатные минералы в четверной координации безусловно является следствием особенностей строения атомов этого элемента. Тот факт, что цинк в двухзарядном состоянии обладает меньшей поляризуемостью, по сравнению с ионами Fe^{2+} и Mg^{2+}, обусловливает понижение химической активности ионов цинка.

В связи с этим, в железо-магниевых силикатах ионы Fe^{2+} и Mg^{2+}, будут связываться прочнее, нежели слабо поляризующиеся ионы цинка.

Таким образом, предположение Г. Нейманна о невозможности изоморфного вхождения цинка в железо-магниевые силикаты также имеет некоторые основания.

Изучение распределения цинка по минералам гранитоидов показало, что цинк действительно концентрируется в железо-магниевых силикатах и, прежде всего, в биотите (табл. 5).

Некоторым исключением является только лейкократовый гранит. В этом образце отмечено высокое содержание цинка в полевых шпатах, что обусловило приуроченность значительной части цинка породы (около 40%) к этим минералам. Однако и в этом случае в биотите наблюдается очень высокое содержание цинка и свыше 50% его приурочено к этому минералу.

Полученные результаты достаточно хорошо согласуются с данными других исследователей. Так для гранита Тоун Маунтин, изученного Санделлом и Голдичем (1953), приводится такое распределение цинка *.

	% цинка породы, приходящийся на данный минерал
Кварц	5
Полевые шпаты	5
Биотит	85

Как видно из табл. 5 содержание цинка в биотитах, являющихся главными темноцветными компонентами изучавшихся пород, более чем в 10 раз превышает содержание цинка в породах. Высокие содержания цинка в биотитах приводятся и К. Х. Ведеполем (1953). Специфическая концентрация цинка в биотитах гранитоидов Сусамырского батолита подтверждается анализами биотитов ряда других образцов из этого района.

	Содержание Zn (в %)
1. Биотит из меланократового плагиогранита (хр. Сарыкамыш)	0,049
2. Биотит из плагиогранита (хр. Сарыкамыш)	0,045
3. Биотит из порфировидного гранита (хр. Джумгол)	0,049
4. Биотит из крупнозернистого гранита (хр. Сусамыр)	0,079

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* Процентный пересчет сделан автором настоящей работы.

Таблица 5

Распределение цинка по минералам каледонских гранитоидов Сусамырского батолита

Минерал	Содержание минерала в породе (в вес.%)	Содержание Zn в минерале (в γ /г)	Кол-во Zn в минерале при пересчете на 1 г породы (в γ)	% Zn породы, приходящ. на данный минерал	Общее содержание Zn в породе (в γ /г)
Неравномернозернистый гранит γ_1^2					
Кварц	35	7	2,5	6	
Полевые шпаты	60,3	10	6,0	15	
Биотит	4,0	870	34,9	87	
Магнетит	0,6	100	0,6	1,7	
Сумма			44,0	109,5	40
Крупнозернистый биотит — роговообманковый гранит γ_2					
Кварц	30	11	3,3	6,3	
Полевые шпаты	65	12	7,8	15	
Биотит	4,2	740	31,2	60	
Роговая обманка	0,75	710	5,3	10,2	
Магнетит	0,25	190	0,5	1,0	
Сумма			48,1	92,5	52
Лейкократовый среднезернистый гранит γ_1^3					
Кварц	32	7	2,2	5,5	
Полевые шпаты	65	24	15,6	39	
Биотит	3,4	620	21,1	52,7	
Магнетит	0,3	230	0,7	2,0	
Сумма			39,6	99,2	40

Таблица 6

Выщелачивание цинка из некоторых каледонских гранитоидов Сусамырского батолита

Образец	Общее содержание Zn в породе (в γ/г)	Колич. Zn извлеченное в результате 2-х выщелачиваний (в γ/г)	Содерж. Zn в остатке после выщелачивания (в γ/г)	Сумма выщелоченного и оставшегося в породе Zn (в γ/г)	% выщелачивания Zn	Примежание
Порфировидный гранодиорит γ_1^2 (хр. Кавак-Тау)	56	38	16	54	67	% выщелачивания взят от общего содержания в породе
Меланократовый адамеллит γ_1^2 (хр. Сарыкамыш)	96	71	9	80	73,5	” ”
Гранит γ_1^2 (хр. Сарыкамыш)	52	45	13	58	78	% выщелачивания взят от суммы выщелоченного и оставшегося в породе
Гранит γ_1^2 (хр. Джумгол)	46	45	6	51	88	” ”
Крупнозерниъстый биотитовый гранит γ_2 ? (хр. Сусамыр)	72	61	11	72	82,5	” ”
Лейкократовый гранит γ_1^3 (хр. Джумгол)	40	38	2	40	94	” ”

Таким образом представление о преимущественной концентрации цинка в железо-магниевых силикатах оказываются совершенно справедливыми.

Вместе с тем, опыты по избирательному выщелачиванию цинка показали, что несмотря на подобную его приуроченность к железо-магниевым силикатам, основная масса атомов этого элемента легко извлекается из породы без разрушения решоток силикатных минералов. Избирательное выщелачивание цинка из образцов исследовавшихся гранитоидов проводился также, как и в случае свинца. Результаты опытов сведены в табл. 6.

В среднем, по данным анализа шести образцов изучавшихся гранитоидов, при подобном выщелачивании извлекается свыше 80% находящегося там цинка. При этом следует заметить, что также как и в случае свинца основная масса растворимого цинка извлекается из породы уже при первом выщелачивании и отчасти при втором. Последующие выщелачивания никакого существенного действия не оказывают. Кроме выщелачивания цинка из пород, было проведено его извлечение из трех мономинеральных фракций биотитов. Во всех случаях оказалось, что при такой обработке из биотитов извлекается от 70 до 80% находящегося в них цинка.

Таким образом опыты показали, что, несмотря на высокую концентрацию цинка в биотитах и других железо-магниевых минералах, последний в настоящее время находится там не в виде изоморфной примеси, а в виде легко-подвижной ("внесиликатной") формы. Приуроченность основной массы цинка к железо-магниевых силикатам может быть объяснена тем, что при кристаллизации магматического расплава цинк действительно входил изоморфно в эти минералы. Высокая температура, существовавшая в то время, облегчала этот процесс, ибо благодаря этой температуре ионы цинка имели большую активность и могли легче входить в решетки силикатов. В дальнейшем, при понижении температуры, эти твердые растворы распадались с высвобождением цинка из решетки. В результате первоначально изоморфно связанный цинк переходил в легподвижную "внесиликатную" форму, оставаясь в кристаллах биотита и других Fe — Mg минералов. С другой стороны, при кристаллизации магматического расплава частично могда иметь место сорбция цинка биотитом.

О минералогическом характере выделений "внесиликатной" формы цинка говорить еще труднее, чем в случае свинца. Возможно, что минералогически эта форма может быть представлена микроскопическими и субмикроскопическими выделениями сфалерита, особенно в тех случаях, когда существенное количество цинка оказывается приуроченным к полевым шпатам. В биотитах же можно ожижать не только наличия субмикроскопических выделений сфалерита, но и атомарного рассеяния цинка.

Приведенные выше данные указывают на то, что в породах в балансе свинца и цинка серьезное значение имеет так называемая "внесиликатная" форма. Легкая подвижность этой части атомов элементов будет иметь особенно большое значение при постмагматических процессах, которые видимо будут приводить в движение значительные количества рудного вещества.

Постмагматические процессы изменения пород обычно развиты значительно шире, чем рудных процесс, и характеризуются очень большим диапазоном физико-химических условий и состава растворов. Естественно, что при всех этих процессах происходит миграция не только основных компонентов, но в еще большей степени — рудных элементов и, в частности, Pb и Zn. Поэтому представляется, что знание условий миграции рудных элементов при этих процессах приобретает первостепенное значение для выявления условий концентрации и рассеяния рудного вещества и в конечном итоге подводят ближе всего к вопросами генетической связи интрузии с оруденением. Несмотря на всю сложность и трудности изучения условий миграции рудных элементов при процессах постмагматического изменения пород это может помочь в разгадке процессе, приводящего к концентрации того или иного элемента и в выработке объективных критериев поисков слепых рудных залежей, что в настоящее время является главной задачей геологии.

Предварительное изучение нахождения свинца и цинка в измененных разностях гранитоидов Сусамырского батолита показало большую сложность этой проблемы. Среди измененных пород наиболее широко распространены разности, претерпевшие низкотемпературное гидротермальное изменение, которое в основном выразилось в серецитизации полевых шпатов и хлоритизации биотитов. Макроскопически эти измененные породы имеют яркокрасную окраску, главным образом за счет гематита, распыленного в полевых шпатах. Обычно в этих разностях не наблюдается существенных изменений в содержании Pb или Zn по сравнению с неизмененными породами. Однако, для ряда образцов было отмечено значительное увеличение содержания свинца (до 80 γ /г породы). При этом следует заметить, что в нескольких случаях подобные резкие повышения содержания свинца были отмечены для пород, которые не несут каких-либо признаков гидротермального изменения (хр. Кавак-Тау). Это дает основание предполагать, что процесс концентрации рудного вещества в данном районе был оторван во времени от процесса постмагматического изменения пород. Как правило, рудные растворы шли по ослабленным зонам гидротермально измененных пород. Однако в ряде случаев этого унаследования не было и рудные растворы, отличавшиеся, видимо, очень слабой химической активностью, или через неизмененные породы, оставляя в них свой полезный груз.

В некоторых районах (Вост. часть хр. Джумгол) отмечаются зоны очень интенсивной гидротермальной проработки гранитов, которая привела не только к полному выносу из пород темноцветных, но даже и к некоторому выносу кварца. Для этих зон характерен вынос Pb и Zn. Например, в одной из таких зон найдено, что в слабо измененных гранодиоритах γ_1^2 содержание свинца и цинка составляет, соответственно, 18 и 58 γ /г породы. В резко измененных же разностях этих пород содержание свинца оказалось равным 4 γ/г, а цинка менее 1 γ.

Изучение характера распределения свинца и цинка в боковых породах рудных месторождений показывает, что в данном районе первичные ареолы рассеяния этих элементов имеют очень незначительные размеры (3-5 м) и видимо довольно точно отвечают зонам концентрации рудного вещества. Подобная локальность первичных ареолов рассеяния может быть объяснена тем, что в районах с относительно слабым развитием рудного этапа растворы поднимались по узким зонам и сбрасывали свой полезный груз в очень небольшом интервале.

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ÉTUDE DE LA RÉPARTITION STATISTIQUE DE L'URANIUM DANS LES GRANITES. CONTRIBUTION À LA PROSPECTION GÉOCHIMIQUE DES GRANDS MASSIFS

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ABSTRACT

L'étude statistique de la répartition de l'uranium et de certains accompagnateurs dans divers granites, permet d'espérer dégager des règles générales sur l'efficacité métallogénique de certains massifs. L'étude est en cours sur plusieurs batholites français.

I—BUT DE L'ÉTUDE

Le service de minéralogie du Commissariat à l'Energie Atomique poursuit depuis des années des études sur le comportement géochimique de l'Uranium dans différents matériaux naturels (roches, eaux, sols, végétaux).

Nos premiers travaux ont été axés vers des objectifs pratiques tels que la prospection géochimique. Les méthodes que nous avons mises au point sont actuellement exploitées avec succès à l'échelle industrielle par une section de Prospection Géochimique dont les travaux vous seront exposés dans une autre communication.

Ceci nous a permis de nous consacrer à des recherches moins directement utilitaires, plus théoriques, et débordant largement sur la géochimie pétrographie.

Nous pensons cependant, que l'accumulation de résultants bien exploités, non seulement sur l'Uranium, mais sur la composition chimique en général des roches, combinée avec une étude pétrographique serrée permettront de guider eficacement le géologue.

Nous nous sommes proposés en premier lieu, l'étude de l'abondance et des lois de répartition de différents éléments dans quelques massifs granitiques français, dont la prospection est déjà avancé et dont les gisements sont relativement bien connus afin de nous servir de base de référence.

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Nous nous bornerons ici à l'exposé de la répartition de l'Uranium, du Sodium et du Potassium dans 3 massifs. Notons en passant que ces travaux ont été menés avec un rythme industriel en tenant compte de certaines réalites économiques.

II—ECHANTILLONNAGE

Une telle étude implique certaines conditions de base qui sont trop souvent négligées.

L'échantillon prélevé doit être *statistiquement et géologiquement* valable. Ceci nécessite une collaboration étroite entre le géologue et le chimiste. La nature pétrographique de l'échantillon doit être déterminée avec exactitude, et l'importance du prélèvement doit être fonction de la grosseur des grains afin d'éliminer les erreurs grossières d'échantillonnage. Enfin, la précision des analyses doit être compatible avec la précision de l'échantillonnage.

Nous avons prélevé les échantillons à une maille aussi régulière que possible de l'ordre de 1 ou 2 kilomètres, soit en affleurement, soit en carrière en essayant d'avoir les parties les plus fraîches.

La grosseur des échantillons a varié de 500 grs. à 5 Kgs selon la structure de la roche.

Une partie de l'échantillon a été gardée pour lames minces. Le reste a été concassé, broyé, soigneusement quarté dans les conditions les plus strictes de propreté, dans un atelier de broyage spécial entièrement du point de vue Uranium.

III—EXAMENS DES ECHANTILLONS

1º)—Du point de vue pétrographique les échantillons ont été examinés macroscopiquement, microscopiquement avec étude à la platine de "Fédoroff" — certains échantillons ont fait l'objet d'une étude en platine intégratrice.

2º)—*Du point de vue chimique:*

a—Tous les échantillons ont été dosés: en Uranium par la méthode fluorimétrique.
b—Tous les échantillons ont été dosés: en Sodium et Potassium par spectrographie de flamme.
c—Un échantillon sur 10 a été dosé pour la Silice.
d—Un échantillon sur 30 a fait l'objet d'une analyse complète de roche (13 éléments).

Distribution des grands Massifs en France.

3º)—*Du point de vue radioactivité:*

a—Tous les échantillons ont été passés au compteur α à scintillation.

b—Tous les échantillons ont été passés au compteur γ quelques analyses de Radium ont été effectuées afin de vérifier l'équilibre U/Ra.

c—Un certain nombre d'échantillons a été examiné par les techniques autoradiographiques.

IV—EXPLOITATION DES RESULTATS

Ceci nous a fourni une masse considérable de résultants bruts portant sur plus de 400 prélèvements.

L'exploitation d'un tel nombre de résultats, implique certaines idées directrices afin d'en tirer une vue synthétique. L'emploi des représentations statistiques classiques procure une aide indispensable. Nous avons ici des "populations" de prélèvements et il s'agit de définir le ou les "caractères" que nous voulons examiner.

Nous avons pris comme caractères, simplement les teneurs en U, en Na_20 et K_20, mais l'emploi de caractères plus complexes nous a donné des résultats particulièrement intéressants mais qui déborderaient trop de cette communication. Une fois le caractère défini, il convient de grouper ensemble les individus qui ont les mêmes valeurs du caractère examiné.

Une première idée qui vient, est d'essayer de répartir les valeurs du caractère sur la carte de prélèvements afin de voir si un groupement par zone géographique se produit, ce qui permet de dessiner les distributions *géographiques* regulières.

Une deuxième méthode moins intuitive est d'étudier la *distribution statistique*. Pour cela on dressa un histogramme de distribution du caractère en groupant les individus par tranches de même valeur.

L'examen de l'histogramme permet en général par un "polissage" de passer à une *courbe de fréquence*. Celle-ci étant considérée comme la représentation géométrique d'une loi idéale de distribution.

L'allure de la courbe suggère en général des *"permanences statistiques"* apparaissant dans les phénomènes les plus divers.

Parmi les lois statistiques les plus courantes, on peut citer la loi normale (Gauss-Laplace), la loi de Poisson et la loi Lognormale.

Cette dernière a pris une importance toute particulière en géochimie, à tel point qu'une loi fondamentale a été proposée par Arhens. Dans une roche donnée: 'la concentration d'un élement est distribuée selon la loi Lognormale".

Cette loi est discutée, nous donnerons dans ce travail notre opinion sur le sens physico-chimique de cette loi que nous admettons pour le moment, comme base de représentation.

En effet, nous verrons au cours de cette étude, ainsi que dans une autre communication, que nous avons une quasi permanence des répartitions en courbe en cloche plus ou moins dissymétrique. La dissymétrie élimine la loi normale: on est amené à choisir la loi Lognormale plutôt que la loi de Poisson, car on dispose de 2 paramètres qui permettent l'ajustement commode des courbes, et de plus la manipulation des calculs est simple.

Loi Lognormale

Si x est la teneur, son logarithme est distribué suivant la loi de Gauss. Ce qui veut dire qu'un échantillon prélevé au hasard à la probabilité:

$$p = \frac{1}{\sigma \sqrt{2 \pi}} \quad e - \frac{(L\,x \;- L)\;\;2}{2\;\sigma\;2}$$

d'avoir une teneur dont le logarithme est compris entre L x et L x + d x. On défini la médiane γ qui est aussi la moyenne géométrique des teneurs

La variance $\sigma^2 = \frac{\pi - 1}{1} \; (Lx - L\gamma)^2$

et l'écart type σ

Nous donnerons donc pour chaque distribution:

la moyenne arithmétique:	am
la moyenne géométrique:	jm
et l'écart type:	σ

V—ÉTUDE SUR LES REGIONS DE VENDÉE ET DE BRETAGNE SUD

Nous avons étudié deux zones, l'une en Bretagne et l'autre en Vendée — faisant partie du massif granitique qui de Parthenay à Nantes, s'allonge suivant une direction Ouest Nord-Ouest et se continue dans toute la Bretagne méridionale par une bande étroite où les caractères deviennent de plus en plus syntectoniques. Le massif granitique de Vendée semble prolonger vers le Nord-Ouest les granites granulitiques du Limousin.

A — BRETAGNE—Massif granulitique de Pontivy

Ce massif s'étend du Faoüet à Pontivy suivant un axe Ouest Nord-Est en se détachant de la bande granulitique qui va de la pointe du Raz à Nantes, puis vers la Vendée. Des prélèvements systématiques ont été faits sur une surface d'environ 500 Km^2.

ÉTUDE PÉTROGRAPHIQUE

Les lames minces faites dans tous les échantillons prélevés montrent une analogie certaine. Il s'agit d'un *granite à deux micas* constitué essentiellement de:

QUARTZ à extinction légèrement roulante ayant parfois, mais très rarement, tendance à être automorphe.

FELDSPATHS POTASSIQUES (microcline) avec microperthites plus ou moins nettes et plus ou moins abondantes suivant les échantillons et parfois màclés Carlsbad. Ce microcline est altéré, il est envahi de petites poussières sphériques ferrugineuses qui se groupent sur les bords en formant une lisière. Souvent il contient du quartz et des plagioclases en inclusions.

PLAGIOCLASES—Ils sont plus ou moins altérés suivant les zones mais relativement constants en composition. Leur valeur moyenne est 29 à 30% d'An mais peut aller de 28 à 32% d'An. Ils sont mâclés suivant la loi de l'albite (0 10).

Comme altération on rencontre des remplissages de poussières ferrugineuses ou de la séricitisation.

LES MICAS—La biotite brune plus ou moins altérée contenant de façon presque constante des inclusions de zircons à auréoles pléochroïques. Ces inclusions atteignent parfois une grande densité. Parfois aussi des inclusions de zircons donnent des auréoles pléochroïques. Cette biotite se chloritise parfois, soit en partie, soit en totalité, exsudant alors Fe et Ti et donnant des enchevêtrements de baguettes de rutile. Dans les zones ou la biotite est entiérement chloritisée on ne voit pour ainsi dire plus d'inclusions à auréoles pléochroïques.

La muscovite, assez fraîche en général est parfois séricitisée sur les bords, de temps en temps a extinction roulante.

La proportion de biotite et muscovite en quantité est à peu près égale avec de temps en temps prédominance de l'un ou de l'autre ou raréfaction des deux.

Accessoires:

APATITE — en quantité très appréciable et parfois en cristaux relativement gros.

ZIRCON —

Un peu de *SPHENE* altéré.

De temps en temps apparaissent des minéraux de métamorphisme, soit que l'on soit en bordure du massif, soit dans l'auréole de lentille de schistes qui

La courbe de fréquence à une allure franchement Lognormale, l'ajustement

L'apparition des minéraux de métamorphisme ne modifie pas la composition des plagioclases mais on y voit alors quelques myrmékites.

DISTRIBUTION DES ALCALINS

La courbe de distribution est donnée à la figure I

Na 10% am = 3.20 %
gm = 3.16 ,,
σ = 0.075
$\frac{\text{am}}{\text{gm}}$ = 1.01 ,,

K 20 % am = 4.8 %
gm = 4.78 ,,
σ = 0.04 ,,
$\frac{\text{am}}{\text{gm}}$ = 1.01 ,,

Les fluctuations autour de la valeur moyenne peuvent être considérées comme faibles.

Sur une centaine d'échantillons analysés trois seulement peuvent être considérés comme anormaux ce qui est confirmé par l'examen pétrographique.

L'étude tant pétrographique que chimique montre une grande homogénéité de la roche sur toute l'étendue examinée même en bordure du massif.

DISTRIBUTION DE L'URANIUM

Les courbes de répartition sont données par la figure II.

U ppm am = 2.31 ppm
gm = 2.05
σ = 0.194
$\frac{\text{am}}{\text{gm}}$ = 1.13

Ce granite peut être considéré comme pauvre en Uranium, la répartition est très voisine de la normale.

Un seul échantillon est statistiquement anormalement fort, et sans rapport géographique avec une minéralisation. Au contraire des prélèvements faits dans de la roche saine à quelques mètres d'une importante minéralisation sont parfaitement normaux.

B — VENDÉE

La zone de nos prélèvements s'étend entre les Herbiers et Châtillon dans une bande granulitique, mordant largement à l'Ouest sur le granite de Mortagne et à l'Est sur le granite de Châtillon. Ce massif est bordé au Nord par les schistes Brioveniens. Ces schistes également sur la bordure Sud (région de Châtillon) mais font place entre les Herbiers et Clisson à un métamorphisme plus évolué: micaschistes et gneiss.

Sur la bordure N du massif les gisements d'Uranium sont encaissés dans le granite (bordure N des granulites) alors que dans le groupe Sud (région des Herbiers), les gisements recoupent les formations métamorphiques au voisinage du contact.

La pétrographie de cette région, s'est d'ailleurs révélée assez complexe et ne correspond que d'assez loin avec le tracé de la carte géologique.

DISTRIBUTION DES ALCALINS (figure III)

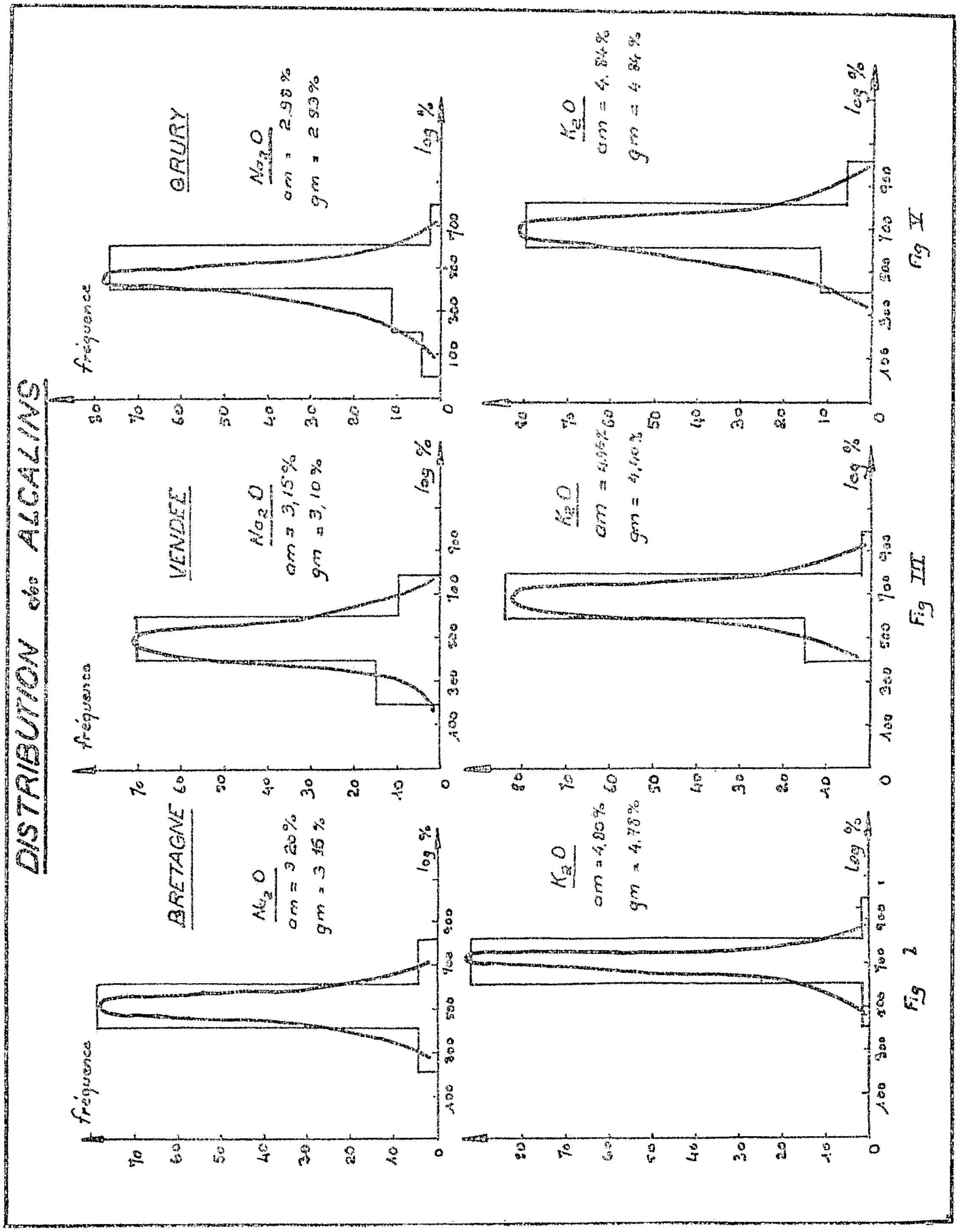
Na 20%	am = 3.15 %		K 30 %	am = 4.46 %	
	gm = 3.17 „			gm = 4.40 „	
	σ = 0.100			σ = 0.160	
	$\frac{am}{gm}$ = 1.01 „			$\frac{am}{gm}$ = 1.01	

L'indice de dispersion est plus élevé qu'en Bretagne ce qui traduit l'existence de plusieurs roches pétrographiquement différentes.

L'emploi de graphique de corrélation avec des caractères plus complexes nous a amené par l'observation de certains "nuages" à distinguer

d'une part —
  tous les échantillons du métamorphisme,
d'autre part, dans les roches à faciès granitique-granulitique
  4 familles que nous avons classées de I à III'.

$R = \frac{Na'0}{K\ 0}$		> 0.8	I
R =		0.65-8	II
R =	0,65	0.55	III
R =		$<$ 0.55	III '


DISTRIBUTION des ALCALINS
BRETAGNE
Na_2O
am = 3,20%
gm = 3,15%
VENDEE
Na_2O
am = 3,15%
gm = 3,10%
GRURY
Na_2O
am = 2,98%
gm = 2,93%
K_2O
am = 4,80%
gm = 4,78%
K_2O
am = 4,15%
gm = 4,10%
K_2O
am = 4,84%
gm = 4,84%
fréquence
log %
0
10
20
30
40
50
60
70
80
100
300
500
700
900
1
Fig I
Fig III
Fig V

Ces paramètres reportés sur la carte des prélèvements permettent un tracé de zones homogènes dont l'intérêt semble prometteur. Nous n'avons malheureusement pas eu le temps de voir dans le détail la correspondance entre cette carte du chimisme des roches et l'analyse pétrographique.

DISTRIBUTION DE L'URANIUM

Aucune répartition géographique régulière n'a pu être mise en évidence et il n'existe aucun rapport entre les teneurs et la présence de minéralisation qui sont ici bien connues.

La courbe de fréquence à une allure franchement Lognormale l'ajustement à une loi Lognormale est d'ailleurs bon. Fig. II

$$\begin{aligned} \text{U ppm} \quad am &= 4.6 \quad \text{pp} \\ gm &= 2.92 \\ \sigma &= 0.235 \\ \frac{am}{gm} &= 1.57 \end{aligned}$$

Ces valeurs sont donc beaucoup plus élevées qu'en Bretagne. Comme nous l'avons dit, des considérations statistiques nous ont amené à distinguer 4 types de roches. Nous avons réparti les teneurs en U par type de roch eet fait pour chaque type la moyenne.

Type	I	sodique	U = 2.2	ppm
,,	II	plus potassique	U = 3.3	,,
,,	III	,,	U = 4.3	,,
,,	IV	potassique	U = 4.9	,,

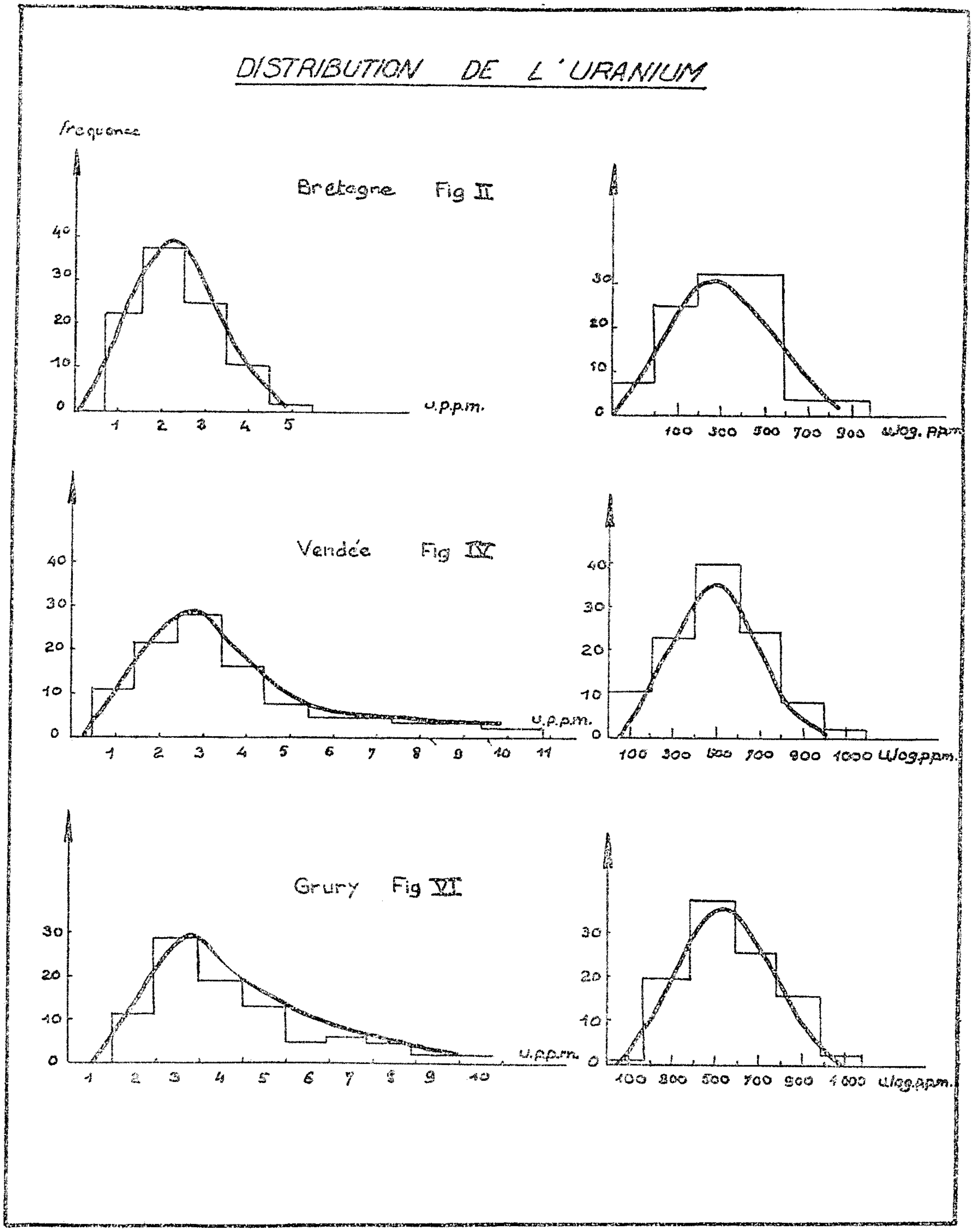
VI—ÉTUDE SU LA REGION DE GRURY (MORVAN)

Le secteur que nous avons étudié appartient à la région du Morvan. Le Morvan est un horst de roches granitiques anciennes formant le relai entre le Massif Central et les Vosges cristallines.

Nos prélèvements ont porté sur les monts de l'Antunois (St. Symphorien) et sur le Morvan méridional où se trouve Grury.

PÉTROGRAPHIE: *La zone* s'étend sur le *granite de Luzy* et ses variantes

Le granite est porphyroïde à grandes orthoses de couleur gris clair ou rose, à gros grains, peu micacés passant localement à un granite à grain moyen ou


DISTRIBUTION DE L'URANIUM
frequence
Bretagne Fig II
40
30
20
10
0
1
2
3
4
5
u.p.p.m.
30
20
10
0
100
300
500
700
900
Ulog. pp
Vendée Fig IV
40
30
20
10
0
1
2
3
4
5
6
7
8
9
10
11
u.p.p.m.
40
30
20
10
0
100
300
500
700
900
1000
Ulog.p.p.m.
Grury Fig VI
30
20
10
0
1
2
3
4
5
6
7
8
9
10
u.p.p.m.
30
20
10
0
100
300
500
700
900
1000
Ulog.p.p.m.

à grain fin non porphyroïde; c'est un type alcalin riche en potasse et en soude, pauvre en chaux.

Ses constituants sont: la biotite, l'orthose, l'albite très abondant, l'oligoclase est presque toujours présent mais en faible quantité. Le quartz souvent englobant, présente localemente des faciès automorphes. Le granite à microcline peu fréquent dans le secteur devient plus abondant dans le Nord où la muscovite apparaît. Ce phénomène est net en bordure de la granulite de St. Léger sous Beuvray.

Le granulite de St. LEGER sous BEUVRAY est considérée par M. Carat, chef du service de recherches de la division de Grury, comme une différenciation de coupole du granite de Luzy. Les porphyroblastes disparaissent en même temps qu'apparaît la muscovite.

L'analyse chimique ne révèle pas de différence essentielle entre le granite porphyroïde et la granulite.

DISTRIBUTION DES ALCALINS

Elle est donnés a la figure V

Na 20% am = 2.98 %
gm = 2.93 ,,
σ = 0.195 ,,
$\frac{am}{gm}$ = 1.01 ,,

K 20 % am = 4,85 %
gm = 4.85 ,,
σ = 0.084 ,,
$\frac{am}{gm}$ = 1

DISTRIBUTION DE L'URANIUM

Quelques zones fortes semblent se détacher sur la carte des prélèvements. Mais le tracé d'une carte d'isoteneurs reste difficile. En tout cas les plages fortes n'ont aucun rapport direct avec les gisements connus.

La courbe de fréquence est donnée à la figure V elle est ici aussi nettement Lognormale:

U ppm am = 5.57
gm = 3.75
σ = 0.203
$\frac{am}{gm}$ = 1.48

VII—INTERPRETATION DES RESULTATS

SENS DES PARAMÈTRES STATISTIQUES

Il est intuitif qu'une simple moyenne arithmétique n'offre qu'un indice central d'un intérêt limité. Il est nécessaire d'avoir en plus la répartition autour de cette moyenne.

De plus dans les distributions dissymétriques apparaît une autre moyenne importante, c'est la moyenne géométrique.

Il s'agit de comprendre le sens de ces valeurs sur le plan géochimique.

La moyenne géométrique représente la valeur la plus fréquente.

La moyenne arithmétique représente l'abondance.

Nous voyons qu'en général ces deux valeurs sont différentes.

L'écart type logarithmique représente à notre avis l'indice de la mobilité géochimique de l'élément étudié.

Nous pouvons voir dans le tableau qui résume ces diverses valeurs pour les trois massifs que les alcalins ont des moyennes assez voisines et des lois de dispersion autour de ces moyennes très différentes: La Bretagne étant un massif homogène, au contraire la Vendée et Grury présentent une pétrographie plus complexe avec des différenciations de roches. L'écart type des distributions permet de chiffrer l'amplitude de ces migrations chimiques à l'intérieur du Massif. Nous voyons au contraire pour l'Uranium des valeurs moyennes très différentes entre les différents massifs et une loi de dispersion qui donne des écarts types relativement voisins.

SENS GÉOCHIMIQUE DE LA LOI LOGNORMALE:

On voit qu'en général la loi Lognormale représente un bon ajustement des courbes expérimentales. Dans certains cas, en particulier pour les alcalins on pourrait hésiter entre normalité et lognormalité. Mains nous considérons systématiquement la normalité comme un cas limite de la Lognarmalité.

En effet, la Lognormalité semble une loi d'un caractère plus général: on sait que l'addition d'un grand nombre de petits effets indépendants engendre une loi normale, or les phénomènes physiques naturels donnent lieu à des réactions d'équilibre chimique de la forme:

$$\alpha \mathrm{A} + \beta \mathrm{B} \rightleftarrows \gamma \mathrm{C} + S \mathrm{D}$$

et la loi d'action de masse nous permet d'écrire entre les variations de concentration des divers constituants:

$$\alpha \frac{dA}{A} + \beta \frac{dB}{B} - \gamma \frac{dC}{C} - \frac{S\,d\eta}{D} = O$$

L'élément différentiel n'est pas dA mais $\frac{A}{dA}$

Monsieur Matheron fait également remarquer que l'affinité" ou énergie libre d'une réaction est une fonction linéaire des logarithmes, des concentrations, des différents constituants.

Dire qu'une répartition est lognormale revient à dire que la répartition des énergies libres est normale, ce qui est logique.

En fait on peut dire comme le fait Monsieur MABILE que la loi lognormale n'est ni un dogme ni une propriété demontrée. Elle peut être considérée comme une sorte de loi physique, qui comme la loi Mariotte pour les gaz rend compte de certains effets. Elle permet d'introduire par des calculs relativement simples des valeurs de référence ayant un sens statistique et géochimique précis, ce qui facilite l'exploitation des résultats et rend possible des comparaisons valables entre des études sur des lieux éloignés.

PROSPECTION DES GISEMENTS D'URANIUM

Il est évident que nous ne cherchons pas à trouver une méthode miracle pouvant désigner à priori les massifs dans lesquels se trouvent des gisements.

La prospection d'un métal fait appel à un faisceau d'informations tant géologiques, pétrographiques, que géochimiques.

Il est evident également qu'une meilleure connaissance de la géochimie d'un élément facilite sa recherche.

Ce qui est d'important en premier lieu dans ce travail, c'est le nombre élevé d'échantillons valables sur lesquels nous avons multiplié les examens et les dosages. Ces échantillons soigneusement conservés peuvent être repris à tout instant pour de nouvelles études.

Nous proposons en deuxième lieu une exploitation statistique de ces résultats, ce qui permet un classement de chaque massif et donne une représentation schématique qui informe sur certaines valeurs remarquables et sur l'amplitude des phénomènes chimiques qui ont pu avoir lieu dans le massif.

Nous ne donnons pas à ces représentation statistiques un sens philosophique précis, mais nous les considérons avant tout comme des outils commodes facilitant comparaisons et extrapolations.

Les représentations géographiques directes de l'U en traces se sont révélées d'un intérêt négligeable; aucune zone métallogénique n'a pu être définie. Nous avons vu dans diverses expériences dans les épontes de filons qu'en l'absence de fissurations, la diffusion latérale ne dépassait pas quelques dizaines de centimètres.

Nous n'avons montré ici qu'un aspect limité de nos recherches qui se poursuivent à la fois sur d'autres massifs et à l'intérieur même de ceux présentés sur d'autres éléments et d'autres modes de représentation.

Nous ne présentons donc pas une méthode de prospection mais plutôt un travail de recherche géochimique mené sur un rythme industriel avec des soucis pratiques qui se rapprochent de ceux que l'on a dans les prospections. Trop souvent en effet les études théoriques de géochimie démarrent sans tenir compte des possibilités analytiques ce qui conduit immanquablement à l'échec ou à la fantaisie, faute de résultats.

Au contraire notre plan de travail est soumis à nos possibilités techniques: capacité de broyage, cadence des analyses... Notre but est évidemment comme pour tout le monde de pouvoir doser le maximum d'éléments dans le maximum de matériaux; mais nous concentrons nos efforts seulement sur les éléments que nous savons doser à la cadence de quelques centaines par semaine. Nous espérons que les quelques résultats que nous avons donnés fourniront déjà des éléments pétrochimiques de base aux géologues de terrain et feront naître des critiques et des remarques utiles à nos travaux ultérieurs.

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PROPOSITION TENDANT A L'ADOPTION D'UNE ÉCHELLE DE TEINTES UNIVERSELLE POUR LA PRESENTATION DES RESULTATS EN PROSPECTION GÉOCHIMIQUE

R. LAMBERT *

RESUME

La lecture, l'interprétation et le rapprochement des cartes d'anomalies géochimiques exécutées dans les diverses régions du globe seraient grandement facilitées par l'emploi d'une échelle de teintes universellement adoptée.

Bien qu'une telle échelle puise ne pas avoir la même portée ou un intérêt pratique aussi généralisé que celle utilisée pour la carte géologique internationale, il semble néanmoins désirable que soit adoptée, dans le même esprit, une échelle de couleurs normalisée, calquée sur celle du spectre.

Une proposition dans ce sens sera soumise au Congrès.

INTRODUCTION

La lecture et l'interprétation des cartes d'anomalies géochimiques seraient grandement facilitées par l'emploi d'une échelle de teintes uniforme, comme cela est de pratique courante dans divers pays en ce qui concerne par exemple la présentation des résultats obtenus en matière de prospection géophysique (cartes telluriques ou de résistivité, en particulier).

Lorsqu'on emploie la dithizone, par exemple dans la prospection de métaux tels que Cu, Pb, Zn, il serait tentant et suggestif d'utiliser pour la présentation des cartes d'anomalies une échelle de teintes qui reproduirait la gamme colorimétrique des variations de teinte de la dithizone suivant la teneur en ppm. du métal contenu. Ce mode de représentation, qui rappellerait l'intensité des anomalies enregistrées, faciliterait notablement la lecture des cartes.

Toutefois, une telle échelle ne serait valable que pour la dithizone; elle ne le serait pas pour d'autres réactifs employés en prospection géochimique, ce qui lui enlève pour la généralité des cas l'interêt qu'elle presenterait pour un réactif déterminé.

Pour pallier cet inconvénient et pour éviter d'employer des échelles de couleurs arbitraires et vàriables, il est souhaitable que la majorité sinon la

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totalité des géochimistes accepte d'utiliser une échelle de couleurs normalisée, que je propose de calquer sur celle du spectre et dans laquelle les valeurs faibles d'anomalies seraient représentées par la couleur correspondant aux radiations de faible longueur d'onde. Les anomalies faibles figureraient ainsi en bleu, les fortes en rouge et les moyennes en jaune, le violet n'étant pas utilisé pour eviter toute confusion avec le bleu.

En faisant varier le degré d'intensité des ces trois couleurs fondamentales, il serait facile d'obtenir une gamme étendue de teintes permettant d'établir un certain nombre de coupures. En cas de nécessité, on pourrait intercaler le vert et l'orangé entre les trois couleurs fondamentales pour les zones à valeurs intermédiaires.

L'échelle proposée aurait le double avantage d'être universelle et applicable quel que soit le réactif employé; elle ferait par ailleurs ressortir des plages à anomalies élevées qui seraient bien mises en évidence par l'enveloppe des plages à tonalités jaunes des zones à valeurs moyennes.

Il va de soi que cette proposition ne vise pas à fixer des normes rigides pour des valeurs déterminées de ppm. mais simplement à adopter une échelle uniforme de teintes en rapport avec l'augmentation des valeurs mesurées et en réservant la possibilité de n'employer, le cas échéant, qu'une partie de l'échelle de teintes ou d'opérer un glissement approprié de cette échelle en fonction des valeurs de ppm. obtenues.

Il n'est pas douteux que cette manière de procéder permettrait une interprétation plus rapide des cartes géochimiques coloriées puisqu'elle éviterait une perpétuelle adaptation aux échelles arbitrairement choisies et faciliterait ainsi les rapprochements et les comparaisons des résultats obtenus dans des régions diverses.

FREQUENCY DISTRIBUTION OF COMBINED ZINC-LEAD-COPPER VALUES IN SOILS OF THE EASTERN UNITED STATES

R. B. FULTON, * R. B. HOY * and
D. L. KENDALL *

ABSTRACT

Frequency distribution histograms and selected areal plots are presented which show the relation of anomalous (over 300 ppm zinc equivalent) to background amounts of metal in soils. Samples were taken in regional reconnaissance in the Eastern United States from Tennessee to New Hampshire, mainly in two lithologic environments; unmetamorphosed Paleozoic carbonate rocks, and Paleozoic metasediments. Assaying, initially performed in local field laboratories, was later done in a central laboratory to which all samples were sent. A dithizone titration was used to determine zinc, lead, and copper, reported as zinc equivalent. Background metal content is lower in both residual and glacial soils which are derived primarily from non-carbonate rocks, than in soils derived from carbonate rocks. While the histograms show that only a small percentage of the soils contain anomalous amounts of metal, the maps show that these high content samples are concentrated in limited areas which form exploration targets. Size and metal content alone are not definitive guides to ore, for anomalies similar in these two respects have been found both related and apparently not related to ore.

INTRODUCCION

Soil samples have been assayed as an aid to prospecting for zinc by the New Jersey Zinc Company on a routine basis since 1949. Results of work in the Eastern United States are presented as frequency distribution histograms with accompanying explanatory texts for areas in Tennessee, Virginia, Maryland Pennsylvania, New Jersey, Vermont and New Hampshire. Examples of typical anomalies show in plan the distribution of the soil metal values in limestone and in metasedimentary terrain.

METHODS

SAMPLING

Areas are selected for sampling on the basis of the occurrence of favorable host rocks for ore. Reconnaissance sampling patterns embrace the presumed

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* *New Jersey Zinc Co., U. S. A.*

favorable formation and slightly overlap adjacent handing and footwall rocks. Sampling patterns designed on the basis of local features, such as attitude of bedding, topography, and accessibility, range from stations one tenth of a mile apart on traverses separated by two hundred feet. Widest spacings are generally used in areas of flatly dipping country rock, and closest spacing is used where dips are steep. Detailed sampling of anomalies found by reconnaissance is customary, but values obtained from detailed sampling are omitted from this report to prevent artificial skewing of the histograms.

Soil samples are collected with an auger or a slotted steel pipe from a depth of two feet to reach "B" horizon of most soils. Samples are collected in a routine manner without regard to soil type, though obviously contaminated areas area avoided.

ASSAYING

In the first soil prospecting by the New Jersey Zinc Company, consideration was given to assaying in the field at the sample sites. The ready accessibility of most areas led to performing the assays in locally established field offices, Assaying in field offices proved satisfactory and was the custom for several years. Later, a central laboratory under supervision of a chemist was established where samples from all areas in the Eastern United States are assayed. Under the central laboratory system the field geologist may devote his energies fully to exploration problems yet receive necessary chemical data with reasonable promptness.

Chemical assay techniques have been modified since 1949 as requirements for accuracy increased. Initially, two generally similar techniques were employed: one, a titrimetric dithizone method developed by B. A. Shippy and others of the New Jersey Zinc Research Departament; the other, a color-comparison dithizone method, evolved by Fulton (1950) from the methods described by Sandell (1944). The latter gave way to an improved titrimetric procedure established by Shippy which is presently being used by the central laboratory. This method detects copper, lead and zinc as an undifferentiated group, reported in terms of zinc and referred to as zinc equivalent.

The assay method is briefly summarized as follows:

> Fifty milligrams of a soil sample which has been dried, crushed and screened through 80 mesh bolting cloth is thoroughly mixed with one gram of potassium pyrosulfate and fused. Ten milliliters of water are added to disolve the fusion product. The resulting solution is transferred to a separatory funnel, buffered with 10 milliliters of citric acid-ammonium hydroxide solution and adjusted to pH 8.3 by dropwise

> addition of ammonium hydroxide in the presence of phenolthalein. This solution is titrated by adding measured increments of 0.0016 percent dithizone-carbon tetrachloride solution, shaking and discarding reacted dithizone until an increment remains green on shaking. The total volume of dithizone solution has been added to the sample is compared with amounts required for standard zinc solutions less the amount required to titrate a blank composed only of reagents. The metal content of the sample is reported in terms of this zinc equivalent.

The aim of soil assaying for prospecting is to obtain semiquantitative results, not the precision usually required in chemical analysis. Laboratory performance is continually checked to insure that this relaxing of classical standards for chemical accuracy does not go too far. Checks are made by introducing soil samples of known zinc equivalent content, representing a wide range of values, unknown to the assayer and marked as field samples. Also, selected field samples are returned to the laboratory for reassay in the guise of routine samples. Results of these checks are reported to the laboratory so that remedial action may be taken to maintain desired accuracy.

FREQUENCY DISTRIBUTION HISTOGRAMS

The histograms, Figures 1.9, illustrate the frequency distribution of metal values in soils in the following geologic environments:

- Limestone areas
  - Tennessee, Ordovician limestone
  - Valley of Virginia, Cambrian limestone
  - Valleys of Maryland and Pennsylvania, Cambro-Ordovician limestone.
  - Valleys of New Jersey, Cambro-Ordovician limestone
  - Valleys of New Jersey, pre-Cambrian Franklin limestrone
  - Valleys of western Vermot, Cambro-Ordovician limestone
- Metamorphic areas
  - Virginia Piedmont, Paleozoic (?) metasediments
  - Northern Vermont Uplands, Cambro-Ordovician metasediments
  - Northern New Hampshire, Ordovician metavolcanics.

While sampling slightly overlaps onto presumed barren hanging and footwall formations, the histograms may be considered to show primarily the distribution of metal values in soils over the ore-bearing formations. In Tennessee, the Virginia Piedmont and the valleys of Maryland and Pennsylvania the soils are almost exclusively residual, and in the Valley of Virginia they are

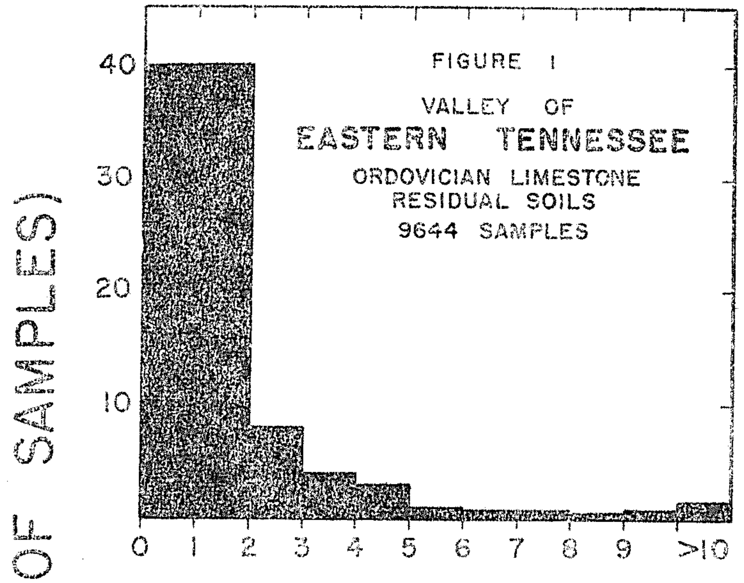


FIGURE 1

VALLEY OF
EASTERN TENNESSEE
ORDOVICIAN LIMESTONE
RESIDUAL SOILS
9644 SAMPLES

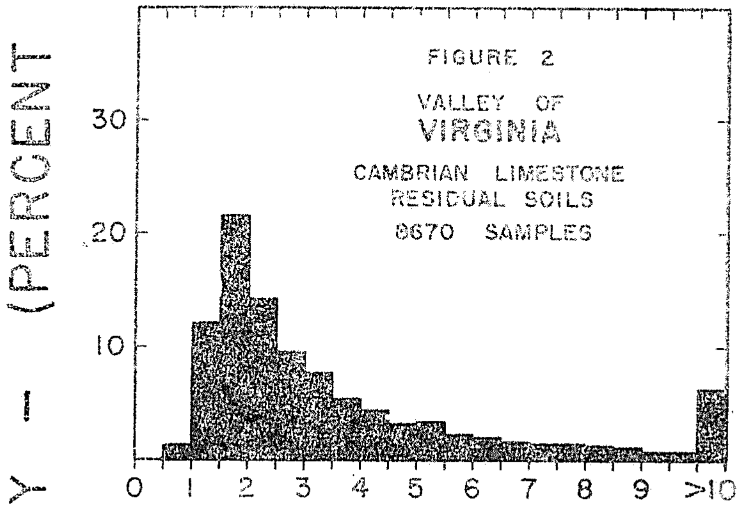


FIGURE 2

VALLEY OF
VIRGINIA
CAMBRIAN LIMESTONE
RESIDUAL SOILS
8670 SAMPLES

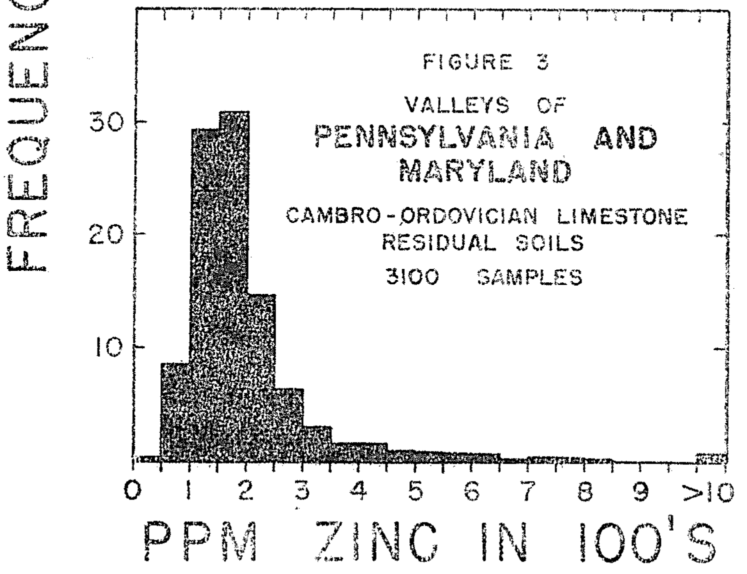


FIGURE 3

VALLEYS OF
PENNSYLVANIA AND MARYLAND
CAMBRO-ORDOVICIAN LIMESTONE
RESIDUAL SOILS
3100 SAMPLES

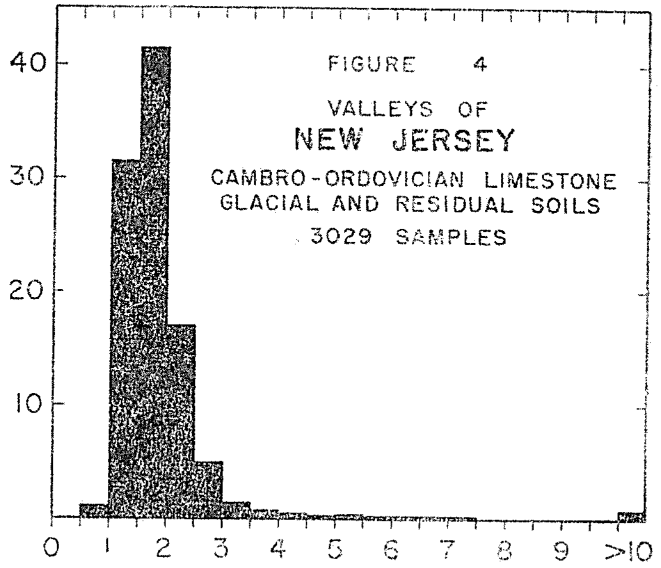


FIGURE 4

VALLEYS OF
NEW JERSEY
CAMBRO-ORDOVICIAN LIMESTONE
GLACIAL AND RESIDUAL SOILS
3029 SAMPLES

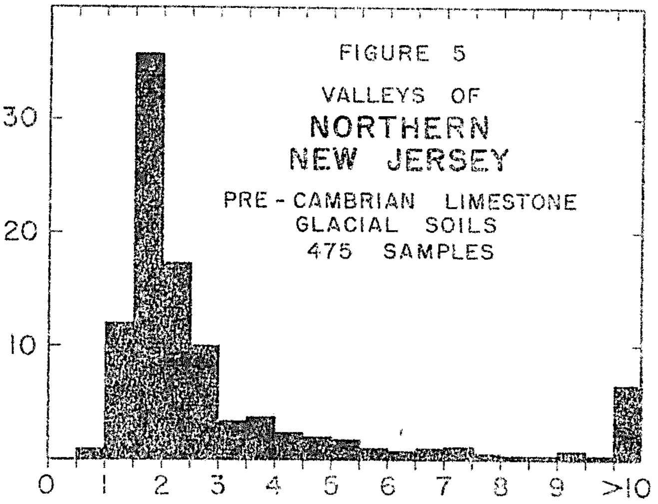


FIGURE 5

VALLEYS OF
NORTHERN
NEW JERSEY
PRE-CAMBRIAN LIMESTONE
GLACIAL SOILS
475 SAMPLES

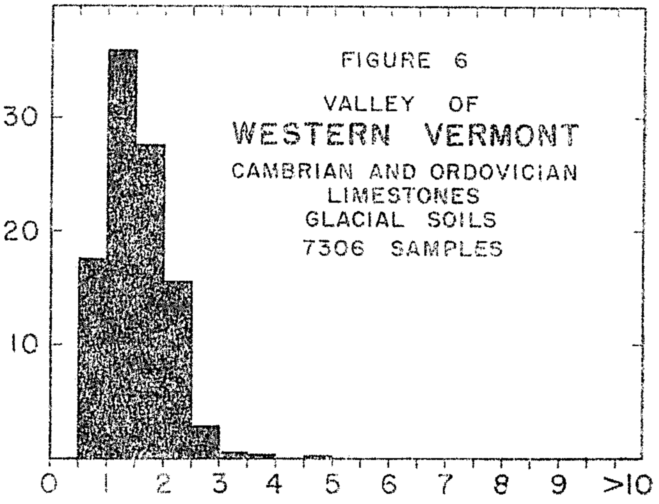


FIGURE 6

VALLEY OF
WESTERN VERMONT
CAMBRIAN AND ORDOVICIAN
LIMESTONES
GLACIAL SOILS
7306 SAMPLES

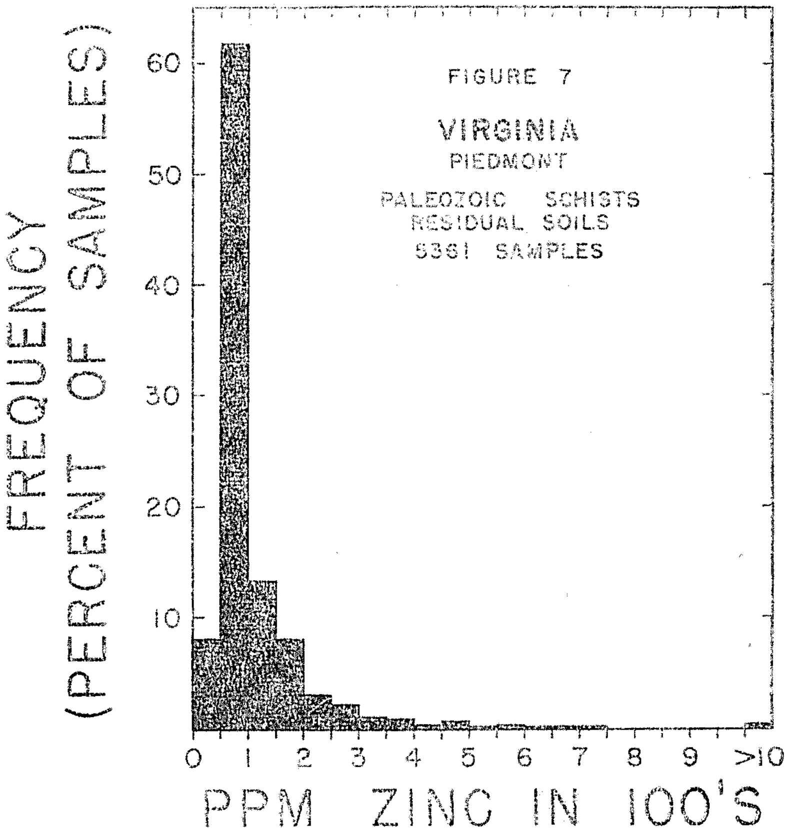
predominantly so. Hence, in those areas the distribution of metal values in the host rock. In the valleys of New Jersey, the valleys of western Vermont and the northern Vermont and New Hampshire uplands, considerable glacial cover may act as a diluent and in places as a mask to the true distribution of metals in the underlying rock. Nevertheless, anomalies significant in exploration have been found in all of these areas.

Geologic summaries of the areas follow:

LIMESTONE AREAS

Tennessee, Ordovician Limestone

Samples were taken from soil overlying the lower part of the Kingsport formation and Copper Ridge in east Tennessee. In the northeast part, the ridge rises rather sharply about 300 feet from the valley floor to a mean elevation of about 1900 feet above sea level. It is unbroken except for a few gaps cut by small streams. Although originally covered with harwood forest, much of



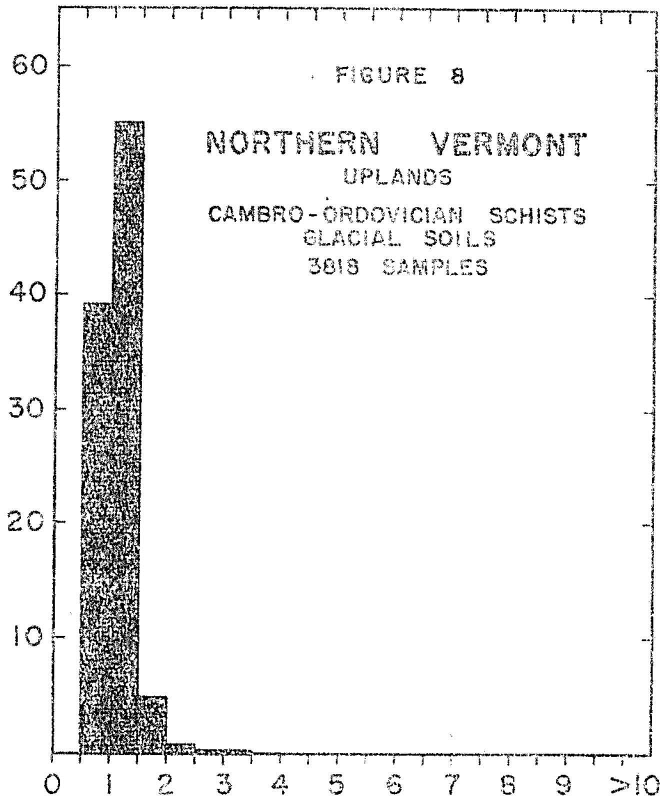


FIGURE 8

NORTHERN VERMONT
UPLANDS
CAMBRO-ORDOVICIAN SCHISTS
GLACIAL SOILS
3818 SAMPLES

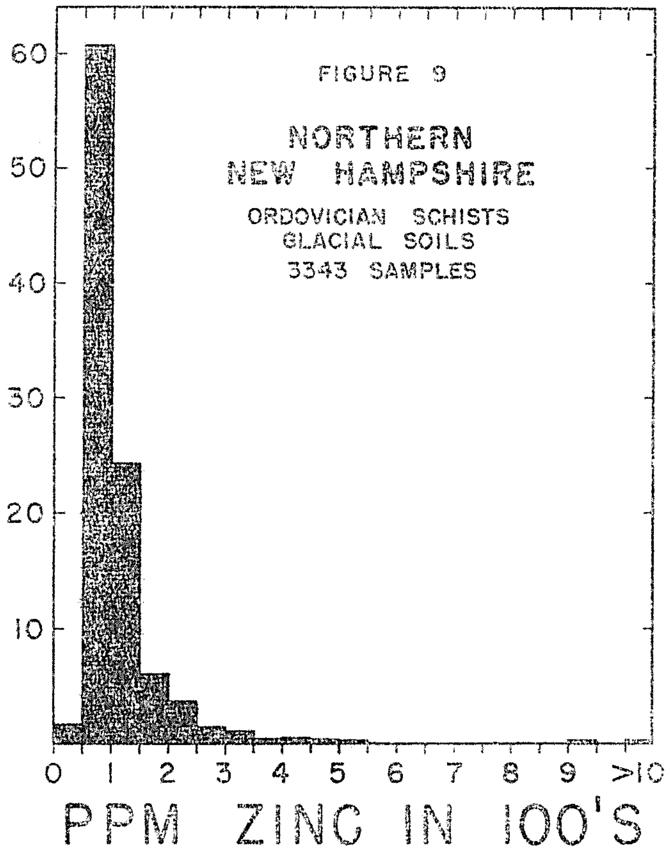


FIGURE 9

NORTHERN
NEW HAMPSHIRE
ORDOVICIAN SCHISTS
GLACIAL SOILS
3343 SAMPLES

the land has been cleared and is now under cultivation. The climate is mild, with an average annual rainfall of 44 inches.

The Kingsport, the ore-bearing formation, lies on the southeas flank of the ridge. Structurally the rocks form a southeast dipping homocline, ranging in dip from about 55° in the northeast part to about 20° in the central part.

The homocline is undisturbed except for minor flexures and cross faults of only a few feet displacement.

Mineralization consists of low-iron sphalerite with coarse dolomite. Deposits are found as breccia fillings in fine (0.02 mm) (Ohle, 1951) dolomite and as replacements in coarse (up to 1.5 mm) (Ohle, 1951) dolomite.

The residual clay ranges in thickness from a few feet to more than 75 feet. Samples were collected at 100 feet intervals along three lines which were parallel to the strike and 200 feet apart.

A histogram, Figure 1, illustrates the frequency distribution of zinc content for 9644 samples. The samples were assayed in field laboratories by the colorimetric method of Fulton, referred to previously. Assays are reported to the nearest 100 ppm zinc as estimated from color comparison standards, and all assays below 300 ppm zinc grouped together. This procedure introduce a slight operator bias which results in clustering of assays around those values for which color standards prepared. For prospecting purposes this bias is insignificant. Because of the difference in assay method the Tennessee histogram is not precisely comparable to the others.

Valley of Virginia, Cambrian Limestone

In the valley of Virginia, Smythe and Wythe counties, soils overlying Cambrian Shady limestone-dolomite rocks were sampled on reconnaissance at stations at 200 ft intervals along lines 500 ft apart perpendicular to strike. These sample lines extended a short distance over the superjacent Rome shale and the subjacent Erwin quartzite. The geology and ore occurrences of this area are described by Currier (1935).

The Valley-floor peneplain, described by Butts (1940) is well developed in the area. Present water courses are intrenched to varying degrees depending on their size and proximity to the New River, the present main drainage. Rounded hills underlain by Rome shale rise above the peneplain surface and the valley is flanked by mountins of Erwin quartzite. Elevation of the intrenched New River is about 1900 ft above sea level, the Valley-floor peneplain is about 2100 ft, and the Rome hills average 2300 ft in elevation, affording in the sampled area a range in relief of about 400 ft.

Soils of the peneplain surface are developed from transported materials which formed a veneer on old residual soils. Erosion has removed this veneer in many place exposing soils residual from the underlying limestone-dolomite rocks. Soils composed of mechanically mixed residual and transported material occur on the side slopes of intrenched streams as a product of mass-wasting, Anomalously high values of zinc occur in the soil of both transported and residual origen. Recent colluvium from the flanking Erwin quartzite mountains is uniformly low in zinc. Soils on the peneplain surface and its dissected slope range in pH from to 5.0. In valley bottoms and poorly drained areas pH is 7.0 to 8.0.

The Shady formation is predominantly dolomite in the area sampled and is locally a hostto ore. The zinc ores occur as sulfide in the dolomite and as zinc silicate at the rock-soil interface. Sulfides in the dolomite occur as replacements and as fracture-willings in rock locally intensely fractured by the action of strike and cross faults (Brown, 1935). The silicate ores and zinc in the soils are the result of weathering of the sulfides.

The histogram, Figure 2, representing samples, shows 80% of the soils to contain less than 500 ppm zinc equivalent and 94% to contain less than 1000 ppm. Though not shown on the histogram, analyses show less than 3% to contain 1500 or more ppm.

Valleys of Maryland and Pennsylvania, Cambro-Ordovician Limestone

The accompanying histogram, Figure 3, represents 3100 samples collected from the valleys of Maryland and Pennylvania. These are the Lehigh, Lebanon, Cumberland, Nittany and Frederick Valleys, lowland areas of fertile farmland with occasional woodlots. Elevations are usually between 300 and 500 ft but range to extremes of 200 to 1500 ft. Sample lines were oriented normal to bedding approximately one mile apart with sample localities spaced at one tenth of a mile. Bedrock consists of Cambro-Ordovician dolomites and limestones which are in general asymetrically folded, overturned to the northwest. Lead-zinc occurrences in the area are described by Miller (1924). The soils sampled are largely residual with a range of pH from 6.0 to 7.0.

Samples were assayed titrimetrically for zinc equivalent. The background compares fairly well with other limestone areas except that a larger percent, 8.5 falls between 50 and 100 ppm. 38 percent of the samples are less than 150 ppm, 69 percent are less than 200 ppm and 94 percent are less than 250 ppm.

Valleys of New Jersey, Cambro-Ordovician Limestone

A suite of 3029 samples from Cambro-Ordovician limestone areas in the Valleys of New Jersey are shown in the histogram, Figure 4. These are largely from Kittatinny Valley, but also included are samples from valleys within the Highlands. Elevation range mainly between 300 to 500 ft with a few hills reaching elevations around 800 ft. Sample lines are oriented normal to strike of bedding one mile apart with sample stations spaced at one tenth of a mile. Bedrock consists of open folded Cambro-Ordovician dolomites and limestones, quartzites covered with glacial soils derived from dolomites, limestones, quartzites and shales. In the inter-Highland valleys glacial soils contain all of the above plus debris from gneisses. Soil pH ranges from 5.5 to 6.5.

Samples were assayed titrimetrically for zinc equivalent. The background is moderately high with only 1.0 percent under 100 ppm, 33 percent less than 150 ppm, 74 percent less than 200 ppm and 91 percent less than 250 ppm.

This frequency distribution in influenced by the relatively high percent of anomalous samples.

Valleys of Western Vermont, Cambro-Ordovician Limestone

The accompanying histogram, Figure 6, depicts 7306 samples collected in the valleys of western Vermont, a lowland area of rolling hills mostly pasture land and woodlots. Elevation are largely between 300 to 600 feet, but occasionally rise to 1000 feet. Sample lines were oriented normal to the strike of bedding, one to two miles apart with sample localities spaced at intervals of a tenth of a mile. Bedrock consists of Cambro-Ordovician dolomites, limestones and quartzites (Cady, 1945) which are overlain by glacial soils derived in large part from the same rock types on strike to the north. The soils consist predominantly of unsorted glacial drift and range in pH from 5.5 to 7.

All samples were assayed in the laboratory titrimetrically for zinc equivalent. The background zinc content is relatively high: 17.5 percent of the samples are in the 50 to 100 ppm range, 53 percent are less than 150 ppm, 81 percent are less than 200 ppm and 97 percent are less than 250 ppm.

METAMORPHIC AREAS

Virginia Piedmont, Paleozoic (?) Metasediments

The area sampled in the Virginia Piedmont is composed of rocks of the Glenarm Series, a term brought into Virginia from Maryland. These are tentatively assigned Paleozoic age. Lithologic banding, considered to be related to original bedding, shows the rocks to be steeply dipping, isoclinally-folded metasediments.

Banding strikes northeast, generally dipping steeply eastward. Prominent foliation also strikes northeastward. Locally the banding is closely folded, and drag folds indicate anticlines overturned to the northeast. Metasedimentary rock-types include: feldspathic chlorite, biotite schist, sericite, quartzite, chlorite amphibole quartzite, and garnet chlorite sericite quartz achist. Within the region, bodies of Ordovician slate occur in the metasediments. The metamorphic grade ranges from chlorite through staurolite zones. Known mineralization in the area generally parallels the strike of the foliation and includes sulfides of copper, lead, and zinc.

Relief in the area is low, ranging from 200 to 463 ft above sea level. Streams from a dendritic pattern with the main water courses flowing southeastwardly perpendicularly to the strike of the beds.

Soils are predominantly residual with some of the gross textures of the original rock commonly preserved in them. There are few rock outcrope except along the largest streams. Overburden averages 75 ft in thckness and ranges up to 100 ft thick. Soil pH determinations range from 3.5 to 5.5.

Samples are collected at a spacing of 200 ft along lines running 30 degrees off strike and spaces 400 ft apart.

Copper, lead and zinc, the ore metals of the district, are detected as an undifferentiated group in the soil assays and are reported as zinc equivalent. The histogram, Figore 7, represents 5372 samples. It shows that 90 percent of the soils contain less than 200 ppm, and 97 percent contain less than 400 ppm zinc equivalent.

Northern Vermont Uplands, Ordovician Metasediments

The histogram represented in Figure 8 illustrates 3818 samples collected in the northern Vermont uplands, a wooded mountainous area of nature topography with elevations ranging from 500 to 2500 ft. Sample lines were oriented normal to the strike of the schistosity, one half mile apart with sample localities spaced at 200 ft intervals. Bedrock consists of Cambro-Ordovician schists and quartzites, which are overlain by generally thin glacial soils derived from similar rock types. The soils contain considerable rock fragments, quartz and mica, and range in pH from 4.5 to 6.

Samples were assayed titrimetrically for zinc equivalent. A high percentage of the assays faill in the lower ranges, 39 percent below 100 ppm and 94 percent below 150 ppm.

Northern New Hampshire Uplands, Ordovician Metavolcanics

A group of 3343 samples, as depicted in Figure 9, were collected in the northern New Hampshire uplands, a forested mountainous area with mature topograhy, and elevation ranging from 700 to 1750 ft. Sample lines are oriented normal to strike of schistosity, 1000 ft apart, with samples spaced at 200 ft intervals. Bedrock consists of Ordovician amphibolites, schists and quarzites which are overlain by glacial soils derived from the sam erock types. A typical zinc deposit is described by Hermance and Mosier (1948). The soils contain numerous rock fragments, quartz, and mica, and range in pH from 5 to 6.

Samples were assayed titrimetrically for zinc equivalent. A high percentage of the samples fall within the lower ranges, 61 percent between 50 and 100 ppm and 85 percent below 150 ppm.

MAPS OF ANOMALIES

Maps of four representative anomalies, Figures 10-13, illustrate typical areal distributions of high values reported in the histograms. Anomalies associated

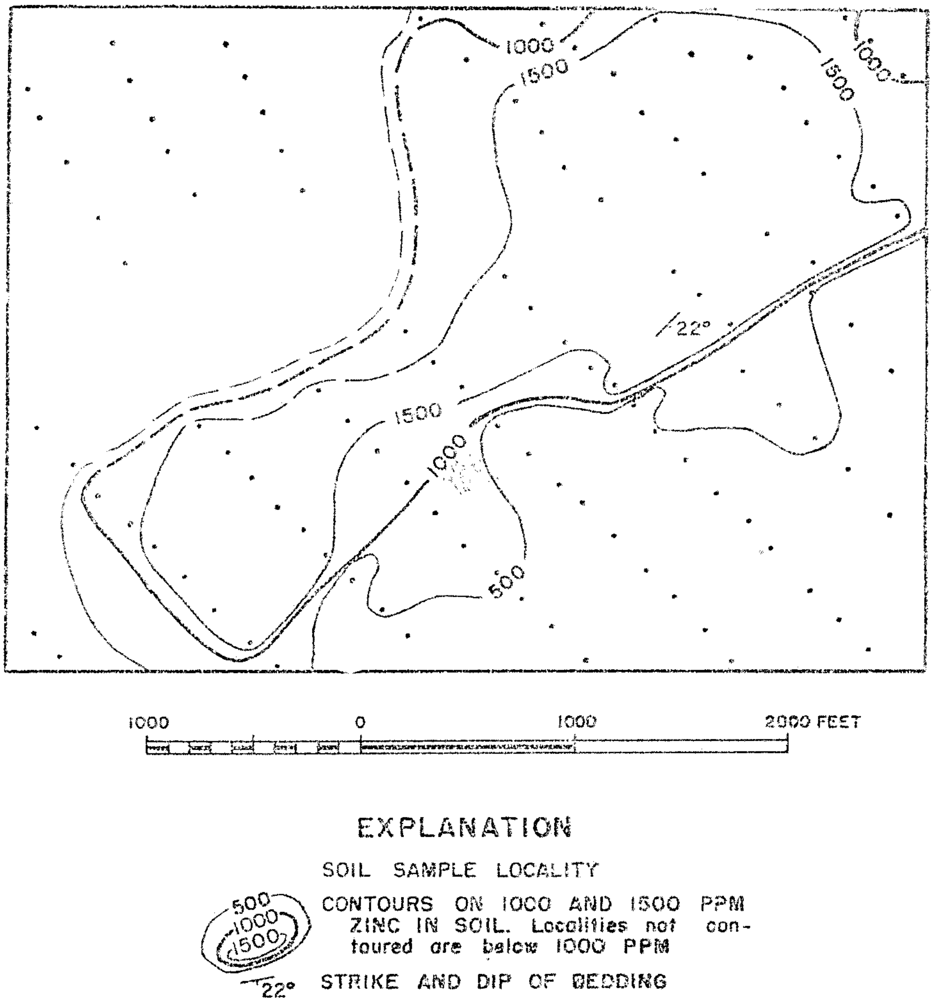


Fig. 10. Soil anomaly associated with known ore in Paleozoic limestone.

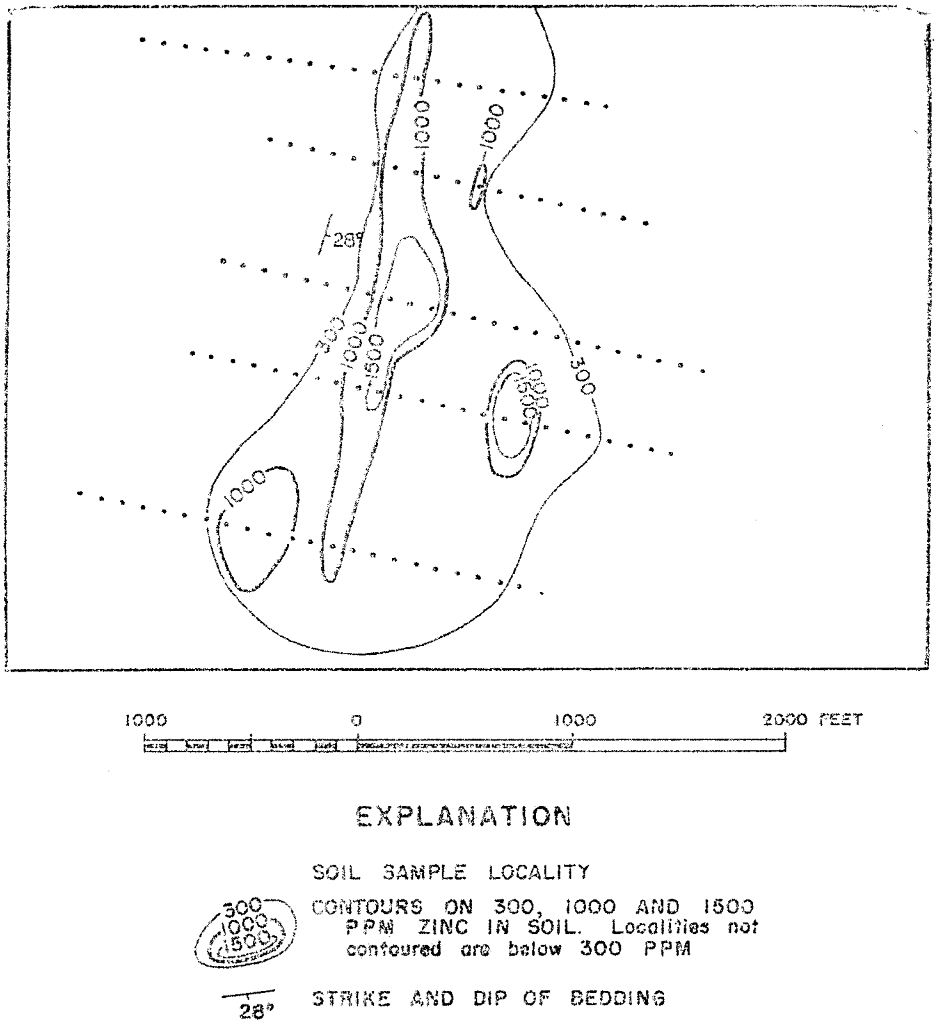


Fig. 11. Soil anomaly in Paleozoic limestone, apparently not associated with ore.

with known ore and anomalies not apparently associated with ore are shown from areas of Paleozoic limestone and Paleozoic metasediments. The maps illustrate the important fact that the few high samples shown on the frequency distribution histograms are geographically clustered together and are apparently related to comparatively local mineralization.

ANOMALIES IN PALEOZOIC LIMESTONE

The map of an anomaly with ore in the Paleozoic limestone, Figure 10, shows high zinc values to be confined to a distinct area The anomalous area is oblong in the direction of strike with the 1500 ppm area extending nearly 4000 feet in length and from 250 to 1500 feet in wdith. The suboutcrop of known ore lies within the 1500 ppm contour.

A map of Paleozoic limestone anomaly apparently not associated with ore, Figure 11, also shows a discrete concentration of high zinc values. The long axis of the anomaly trends essentialy parallel to the strike of bedding with the 1000 ppm area being 2700 feet long and from 100 to 350 feet wide. The anomaly was investigated by eleven diamond drill holes, which found only traces of zinc-lead mineralization. The up-dip projection of the mineralized beds to the surface falls within the 1000 ppm area.

In the two examples chosen, Figure 10, the anomaly associated with ore, is of larger area and higher mineral content than Figure 11, the anomaly apparently not associated with ore. But larger area and higher mineral content are not conclusive evidence of ore. Other examples could be given where anomalies larger

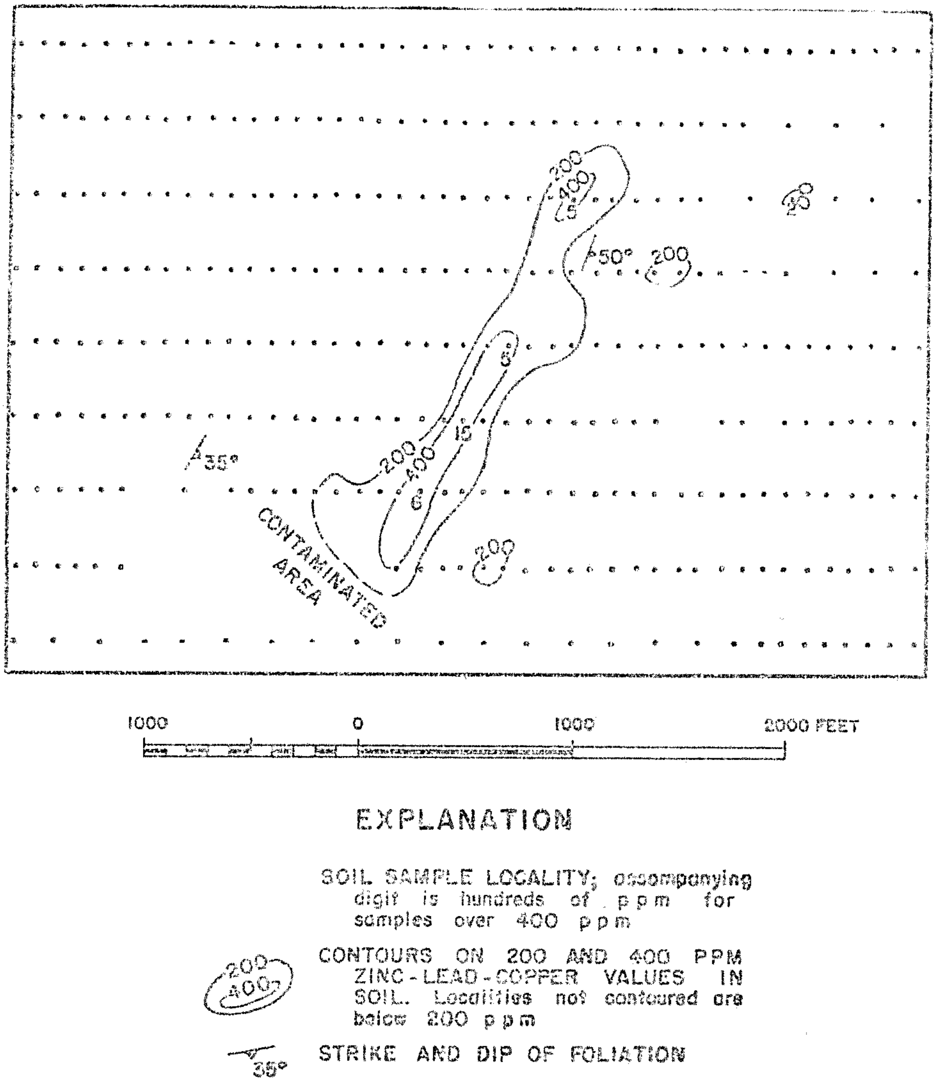


Fig. 12. Soil anomaly associated with known ore in Paleozoic metasediments.

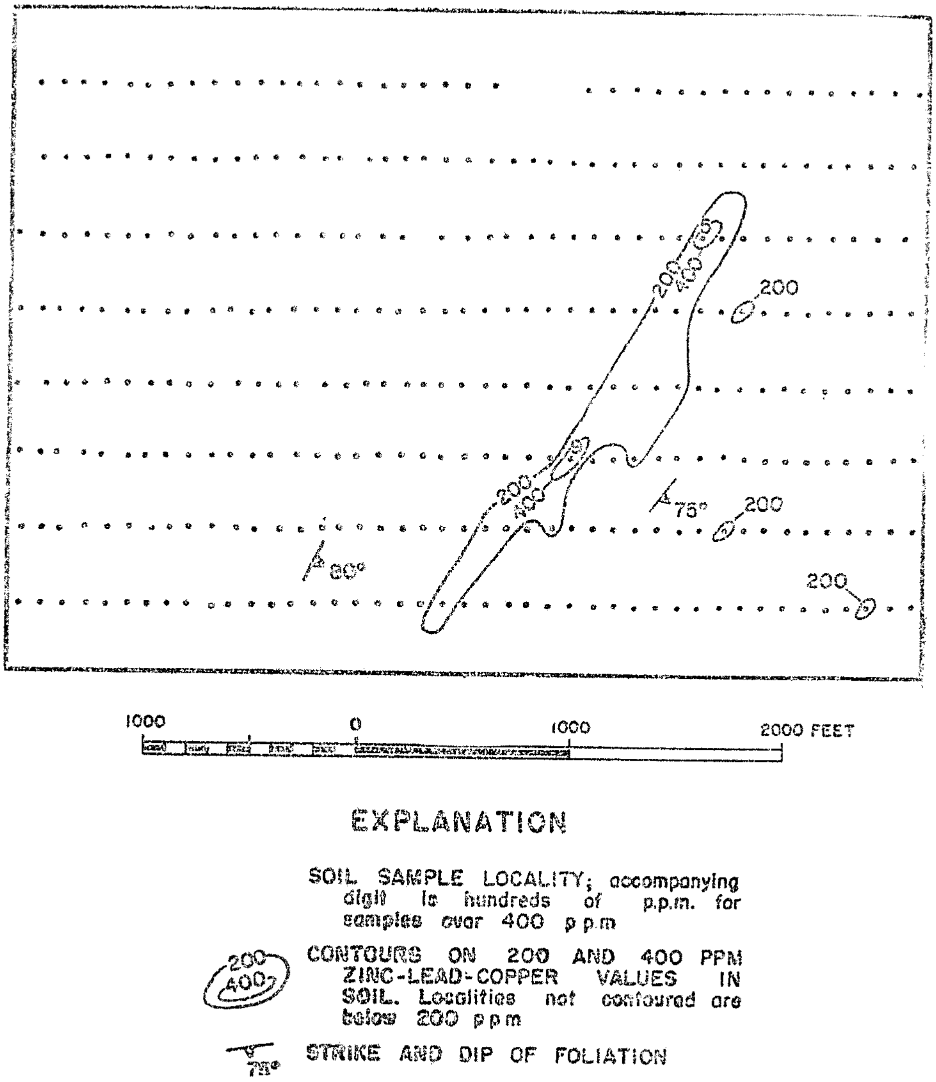


Fig. 13. Soil anomaly in Paleozoic metasediments, apparently not associated with ore.

than Figure 10 have been drilled with negative results and anomalies smaller in area and of lower zinc content than Figure 11 were found to be associated with ore.

ANOMALIES IN PALEOZOIC METASEDIMENTS

An anomaly associated with known ore in Paleozoic metasediments is shown in Figure 12. It is elongate in the direction of strike of foilation, being at least 2000 ft long and varying from 200 to 400 ft in width. Within the 200 ppm area is a discontinuous core of values over 400 ppm, which also appears elongate parallel to strike. The exact length of the natural anomaly is not now determinable because of mine dump contamination at one end.

An anomaly which is apparently not associated with ore is shown in Figure 13. It is similar in shape and size to the anomaly associated with known ore, Figure 12, described in the preceding paragraph. It is about 2400 ft long, with its long axis parallel to strike, and ranges in width from 150 to 350 ft. It, too, has areas higher than 400 ppm, but they are less extensive than those in Figure 12.

The two anomalies are in the same lithologic enviroment and are less than 3000 ft apart. The similarity of the two maps illustrates the difficulty in interpretation of anomalies as guides in ore search. Apparently simple areal distribution of the most prominent base metal values is not the only criterion necessary to evaluate anomalies.

CONCLUSIONS

Study of the data leads to the following conclusions:

1—Background metal content is lower in both residual and glacial soils which are derived primarily from non-carbonate rocks, than in soils derived from carbonate rocks.

2—Background metal content in both glacial and residual soils in areas of carbonate rocks is approximately the same in the six carbonate areas sampled. of mineralization in a particular region; hence, greater skew would indicate a region having greater mineral potential.

3—Background metal content in both glacial and residual soils in areas of non-carbonate rocks is approximately the same in the three metamorphic areas sampled.

4—Study of frequency distribution of soil metal values provides a means of distinguishing background from anomalous metal content, and permits the determination of that value marking the threshold of interest in exploration. This latter value may vary with geologic environment. Such factors as ore habit, structure, rock-type, climate and topography must be considered.

5—It is possible that compilation of frequency distribution histograms may be an aid to classification of regions with respect to exploration potential. The amount of skew of distribution toward the high side may be related to the amount

6—Comparison of frequency distribution data with geographic distribution indicates a pronounced areal concentration of high values. While the histograms show only a small percentage of the soils to be high in metal content, the maps show that the high values are concentrated in limited areas which form targets for exploration.

7—The distribution data on the four maps shows that concentration of metal values is not a definitive guide to ore. Geographic distribution of soil metal values may appear similar in two cases, yet one may be related to ore and the other may not be obviously so associated. Exploration of soil anomalies should be based on further study of the geologic origin of the anomaly.

ACKNOWLEDGEMENTS

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ÉTUDE STATISTIQUE DE LA DISPERSION GÉOCHIMIQUE DE L'URANIUM DANS LES SOLS

R. COULOMB

ABSTRACT

The geochemical prospecting in soils has reached at the CEA a high degree of technical improvement in its tactical use.

The statistical study of anomalies and the fitting of distributions to a lognormal law give valuable qualitative information and the ability of defining objective numerical parameters, comparable from a district to another.

Strategical prospecting, with large sample interval, in unknown areas, can be undertaken with those studies as a basis.

GENERALITÉS

La prospection géochimique dans les sols a atteint au CEA un degré de perfectionnement technique très élévé dans son emploi tactique, e'est-à-dire à une maille de prélèvements de quelques dizaines de mètres.

Cependant, un progrès décisif serait encore fait si l'on pouvait généraliser cette méthode à un emploi stratégique.

Mais, alors que dans le cas de prélèvements serrés, le choix de certaines valeurs critiques (teneur fondamentale, teneur limite des isogrades, etc...) est intuitif, seule la définition de paramètres statistiques objectifs, comparables de région à région, peut donner une solution valable aux prospections de grands spaces avec un nombre limité de prélèvements.

L'étude statistique que nous avons faite sur les résultats déjà acquis montre que l'on peut définir facilement des paramètres numériques ayant un sens statistique et géochimique précis.

L'étude des histogrammes de distribution des teneurs et l'ajustement dans la plupart des cas à une loi lognormale fournissent des renseignements qualitatifs précieux sur le mécanisme physico-chimique de migration et de distribution de l'uranium dans les sols des régions granitiques.

Nous essayons de dégager un certain nombre de règles permettant d'envisager des prospections à grandes mailles (à l'échelle d'une formation géologique) ne démarrant plus obligatoirement sur des points connus.

Nous donnons en annexe quelques éléments de statistique. Ce rapport ne fait intervenir pratiquement que des notions simples et classiques.

HISTOGRAMMES DE DISTRIBUTION

Nous avons travaillé sur des résultats fournis par six campagnes de prospection. Les dernières campagnes exécutées par la section de M. Grimbert comportent un nombre considérable de prélèvements.

Le tableau I donne la repartition des effectifs par tranche de teneur de 1 ppm.

Les histogrammes de fréquence de 1 à 6 résument ce tableau.

Nous avons classé les courbes de fréquences de la Crume à Verneix par ordre de déformation croissante, la courbe de la Crume étant en cloche, symétrique et très pointue, la courbe de Verneix étant très dissymétrique et étirée vers les fortes teneurs. L'allure générale des courbes autres que la Crume suggère une loi lognormale.

AJUSTEMENT À UNE LOI LOGNORMALE.

Nous avions d'abord ajusté très grossièrement sur papier semi-logarithmique les distributions, cela paraissant plus commode et plus représentatif.

Nous avons été amenés par des considérations de géochimie à attribuer à cette loi de distribution une importance particulière et même une valeur de critère de l'existence d'un phénomène de dispersion géochimique.

Pratiquement, nous avons découpé les logarithmes des teneurs en classes d'amplitude 0,260.

Nous avons vérifié l'ajustement des cinq campagnes (La Crume mise à part) à une loi de Gauss par le test de la droite de Henry (Fig. 7).

TABLEAU I

ppm	La Crume		La Chapelle Largeau		Le Balai		Arfeuille I		Arfeuille II		Verneix	
	eff,	pour cent	eff,	pour cent	eff,	pour cent	eff	pour cent	eff	pour cent	eff	pour cent
1	2	2,4	15	2,3	30	1,9	2	1,6	13	7,6	8	1,1
2	15	18,4	188	29,2	230	14,4	40	33	38	22	72	9,6
3	48	58,5	195	30,2	345	21,3	33	27	41	36,5	86	11,4
4	12	14,6	128	19,9	340	21,2	16	13,2	21	12	102	13,5
5	2	2,4	63	9,7	210	13,2	12	9,9	25	14,6	79	10,5
6	2		28	4,3	115	7,7	8	6,6	9	5,2	47	6,2
7	1		14	2,1	85	5,3	2	1,6	5	3	53	7
8	82		6	0,9	45	2,8	1		5	3	45	6
9			8	1,2	22	1,4	2		5	3	31	4,1
10			6		15		2		3	2	36	4,8
11			4		18				1		35	4,7
12			1		10		2		1		29	3,8
13			1		20		122				23	3
14			1		6				1		14	
15			2		12						21	
16			647		7						8	
17					18						8	
18					10						9	
19					3				1		3	
20					7				173		10	
21					3						6	
22											6	
23											5	
24					5						6	
25											6	
26					24						6	
27					14						6	
					1,594							
100												

TABLEAU II

EXEMPLE SUR VERNEIX

Limite de classe	Effectifs	Effectifs cumulés	Fréquence cumulée	Classes correspondant à la loi normale réduite
— 00	8	8	0,0104	— 00
—				—
0,130	72	80	0,1045	— 2,31
0,390	188	268	0,3499	— 1,26
0,650	224	492	0,6423	— 0,38
0,910	168	660	0,8620	— 0,37
1,170	82	742	0,9687	1,09
1,430	17	759	0,9910	1,85
1,690	7	766	1,00	2,33
+ 00				+ 00

Seul l'ajustement de la distribution des teneurs du "Balai" n'est pas excellent, mais il semble qu'il y ait superposition de deux populations lognormales de paramètres différents dont nous verrons l'explication plus loin.

ANALYSE DES DISTRIBUTIONS.

Loi lognormale.

Si x est la teneur, son logarithme Lx est distribué suivant la loi de Gauss, ce qui veut dire qu'un échantillon prélevé au hasard a la probabilité d'avoir

$$p = \frac{1}{\sigma\sqrt{2\pi}} \; e^{-\frac{(Lx - L\mu)^2}{2\sigma^2}} \; d\,(Lx)$$

une teneur dont le logarithme est compris entre Lx et Lx + dx.

On définit: la *médiane* μ qui est aussi la moyenne géométrique des teneurs:

$$L\mu = \frac{1}{n} Lx$$

50 pour cent des teneurs sont inférieures à μ, 50 pour cent supérieures.

La variance σ^2.

C'est la variance des logarithmes des teneurs.

$$\sigma^2 = \frac{n - 1}{1} \quad (Lx - L\mu)^2$$

L'écart type σ.

TABLEAU III

EXEMPLE DE CALCUL SUR LA CHAPELLE LARGEAU

Valeur centrale x	Effectif	n x	x — x	$(x—x)^2$	$n(x — x)^2$
0,260	203	52,6	0,255	0,065	13,145
0,520	325	169	0,005	0,00003	0,0065
0,780	111	86,6	0,265	0,070	7,76
1,040	21	21,8	0,525	0,274	5,66
1,300	2	2,6	0,785	0,63	1,26
	647	332,6			27,88

$x = 0,641$ $\mu = 3,27$

$\sigma^2 = 0,431$ $M = 2,86$

$\sigma = 0,204$

Le tableau suivant peut ainsi être dressé.

TABLEAU IV

Campagne	am p.p.m	μ'	μ = gm p.p.m.	σ
La Crume	3,08	0,480	3,02	0,134
La Chapelle	3,81	0,515	3,27	0,204
Arfeuille I	3,60	0,517	3,29	0,244
Arfeuille II	3,90	0,560	3,65	0,284
Le Balai	6,36	0,641	4,37	0,290
Verneix	11.1	0,803	6,31	0,330

INTERPRÉTATION GÉOCHIMIQUE

IMPORTANCE DES VALEURS TYPIQUES.

Nous voyons dans le tableau IV des centaines de résultats des prospections géochimiques synthétisés par un petit nombre de valeurs dont il faut comprendre le sens géochimique.

Les moyennes: La dissymétrie des courbes introduit deux moyennes importantes: la moyenne arithmétique classique (am) et la moyenne géométrique (gm $= \mu$).

—La moyenne géométrique représente la valeur la plus fréquente.

—La moyenne arithmétique représente l'abondance de l'U dans le secteur considéré.

La teneur en U à l'origine n'est pas nulle. En fait il existe une teneur fondamentale à l'echelle d'une formation géologique qui depend de la nature de la roche sous-jacente et non de la présence de gisements. Si plusieurs campagnes sont faites sur les mêmes formations, on peut admettre que les courbes théoriques ont un point commun à l'origine qui passe par cette teneur fondamentale.

Nous considérons la moyenne géométrique comme un paramètre de référence de chaque campagne locale qui nous sert à la détermination du premier isograde.

L'ecart type σ est un indice de dispersion statistique mais également est un indice de la mobilité géochimique de l'U pour chaque secteur géographique local.

Il apparaît une relation qui n'était absolument ni évidente, ni obligatoire a priori et que nous n'avions pas vue.

En effet, en général μ (gm), et σ sont deux paramètres indépendants qui suffisent à définir une loi lognormale. Mais si diverses campagnes ont lieu sur des régions à teneur fondamentale constante comme celles que nous avons étudiées, μ et σ varient alors dans le même sens.

Ceci veut dire que, dans une même région géologique, les anomalies *fortes en teneur* ont aussi une grande dispersion, c'est-à-dire *une large auréole.*

Ainsi, un quadrillage beaucoup plus lâche que celui que nous employons ne peut pas manquer les anomalies importantes (alors que nous avions peur de laisser passer des anomalies fortes en teneur et faibles en surface).

Nous avons cherché une explication théorique à ce phénomène.

SIGNIFICATION GÉOCHIMIQUE DE LA FORME DE LA LOI DE RÉPARTITION

Nous venons de définir un certain nombre d'indices statistiques et géochimiques.

Il est intéressant également d'interpréter la normalité ou la lognormalité de la courbe de fréquence.

La Crume, par exemple, donne une répartition en première approximation *normale* et peu dispersée.

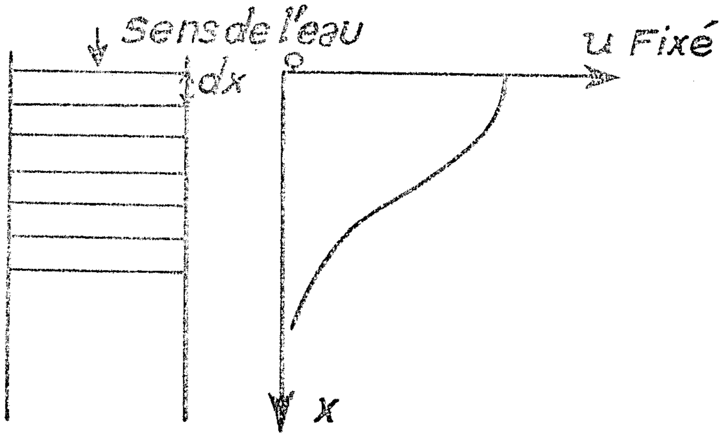
Cette forme de courbe est le critère de *l'absence de phénomène de dispersion* géochimique d'uranium dans le cycle d'altération.

L'étude de la répartition et de la dispersion de l'uranium dans les roches elles-mêmes est en cours. Les phénomènes de migration donnent lieu également à des lois lognormales, mais l'amplitude des dispersions dans les roches ignées est très faible devant l'amplitude des dispersions dans le cycle d'altération.

En effet, sur une roche qui contient un peu d'uranium comme le granite. le sol dérivé (en l'absence de transport mécanique important) contiendra également un peu d'uranium, mais selon une distribution au hasard. Mais, de plus, la fluctuation de teneur de la roche d'un batholite par exemple n'étant pas cosidérable et l'uranium se trouvant sous une forme chimiquement peu mobile, *la dispersion sera faible.*

Au contraire, nous considérons tout histogramme dissymétrique étiré vers les fortes teneurs et ajustable à une loi lognormale comme la preuve d'un *phénomène de circulation* chimique de l'uranium et de fixation par échange d'ions dans les sols.

En effet, si l'on découpe des tranches dans une colonne de sol sur laquelle on a fait passer de l'eau contenant de l'uranium, la teneur de chaque tranche donne une courbe dont l'allure est donnée par le schéma ci-joint.



La forme exacte de la courbe dépend de la *nature* du sol et de la *teneur* en uranium de l'eau qui circule (de son pH, de sa température, etc...).

La transposition à l'espace de l'allure de la courbe sur colonne élémentaire peut faire saisir intuitivement l'intervention d'une loi logarthmique.

On comprend également que, si dans un même secteur on a plusieurs systèmes de circulation d'eau à différentes teneurs dans le même sol, on obtient plusieurs populations lognormales de paramètres différents dont la superposition n'est pas lognormales (cas du Balai).

Nous sommes ici dans un cas où vraiment la lognormalité est expliquée parfaitement par l'application de la loi d'action de masse entre les variations de concentrations entre chaque tranche de la colonne échangeuse.

La forme des anomalies, l'absence de niveaux pédologiques préférentiels, l'allure des courbes de répartitions ne pourraient s'expliquer par des phénomènes de précipitation ou de transport mécanique. Elles seraient difficilement explicables par un phénomène d'échange cations dans le sol. Au contraire l'échange anion beaucoup moins brutal donne une solution satisfaisante. Or l'U est un élément très mobile dans le cycle d'altération sous la valence VI, et il circule dans la nature le plus souvent sous forme de complexe anion soit complexe carbonate, soit complexe sulfate. Nous voyons donc qu'un bon accord peut être ainsi établi entre les données expérimentales et théoriques.

CONCLUSIONS PRATIQUES

Dans les espaces non prospectés mais de structures géologiques analogues à celles que nous avons rencontrées, l'ordre du travail pourrait être le suivant:

1°) *Détermination de la teneur fondamentale* géologique par 50 ou 100 prélèvements au hasard dans toute la formation.

Les prélèvements tombant dans une zone uranifère ont peu de chance d'être nombreux.

On obtient donc une courbe de dispersion analogue à celle de la Crume et on définit la teneur fondamentale par la moyenne arithmétique M' et la dispersion σ' par l'écart type des teneurs (pas de logarithmes dans ce cas).

2°) *Recherche d'un fil directeur.* On effectue alors des quadrillages ou des profils systématiques à grande maille (plus de 500 m) en utilisant au mieux ce que l'on peut connaître de la géologie régionale et ce que l'on sait des propriétés générales de l'uranium (concentration dans les creux, étirement des anomalies dans le sens de circulation des eaux, etc...).

Tout point dont la teneur est $M' + 2\,\sigma'$ a en gros 95 pour cent de chance d'être une *anomalie géochimique valable* (au moins aussi valable qu'un point "fort" au compteur) et des prélèvements complémentaires s'imposent.

On gardera présent à l'esprit que, contrairement à la radioactivité, un "point" géochimique anormal a plus de chance de faire partie d'une anomalie "forte" (en teneur et en surface) que d'une "petite" anomalie puisque teneur, surface et importance de l'injection uranifère sont liées.

3°) *Recherche des secteurs les plus favorables.* A partir des points anormaux, le quadrillages s'orientera par panneaux de 50 à 100 prélèvements à maille toujours assez lâche.

Les histogrammes de chaque panneau et les moyennes géométriques seront alors les guides principaux.

Les histogrammes symétriques à moyenne géométrique proche de la teneur fondamentale seront rejetés. Au contraire, le quadrillage sera orienté vers une dissymétrie maximale.

4°) *Carte d'anomalie.* Lorsque les secteurs favorables auront été dégrossis, le *quadrillage tactique* permettra le tracé des anomalies. Il sera cependant intéressant de voir si les anomalies s'ajustent à une loi de dispersion lognormale ou si un découpage convenable ne fait pas apparaître plusieurs populations pouvant être interprétées par des systèmes de circulation d'uranium différents.

En résumé: les idées suggérées par l'étude statistique d'un nombre déjà important de campagnes ont besoin d'être essayées concrètement sur le terrain, ce qui, à la cadence de travail de la section de prospection géochimique, peut être fait très vite.

Bien qu'audacieuse en apparence, cette conception de la prospection de grands espaces repose sur des bases statistiques et géochimiques beaucoup moins hasardeuses que la découverte en prospection volante d'un point radioactif dans une région pauvre en affleurements.

Ce procédé de prospection ne peut être envisagé que parce que le C.E.A. est actuellement le seul organisme au monde à disposer d'une méthode de dosage de terrain gardant, malgré son haut rendement et son bas prix, une bonne précision.

ANNEXE

MATERIEL STATISTIQUE ELEMENTAIRE

Nous avons largement emprunté à l'ouvrage de J. Mothes auquel nous renvoyons pour une théorie plus complète.

1.—TERMINOLOGIE

1.1—POPULATION ET INDIVIDU.

On entend par population l'ensemble des individus soumis à examen, par individu, chaque unité de la population qu'on est amené à considérer isolément lorsqu'on se propose de procéder effectivement à une observation.

Les deux termes ont un sens beaucoup plus large que dans le langage commun. Nous parlons ici de population de prélèvements.

Une population n'est définie qu'après détermination de ce que l'on se propose d'observer, c'est-à-dire qu'après définition du *caractère* à examiner, ici la teneur en uranium du prélèvement.

1. 2—NOTION DE CARACTÈRE.

Quand on examine un groupe d'objets, la propriété qu'on décide d'observer est généralement désignée sous le nom de caractère. Il faut que ce caractère puisse prendre des valeurs variables.

Les valeurs du caractère sont mesurées par une technique convenable (mesure physique ou analyse chimique).

Ceci pose le problème délicat de l'erreur de mesure. Chaque résultat de mesure x étant la résultante de 3 termes:

$$x = X_o + E_s + E_a$$

X_o étant la valeur *vraie*
E_s étant la part d'erreur systématique
E_a étant la part d'erreur accidentelle.

Une mesure doit donc être examinée sous l'angle de sa *justesse* (accuracy) et de sa *précision*.

Les valeurs que nous donnons dans ce rapport sont les valeurs observées x.

2.—PRÉSENTATION DES DONNÉES

Lorsque les N individus soumis à l'observation ont été observés, il s'agit de présenter correctement les résultats.

2. 1—NOTION DE DISTRIBUTION STATISTIQUE.

La première opération consiste à grouper ensemble les individus qui ont les mêmes valeurs du caractère examiné.

On obtient ainsi une "distribution statistique", ou "distribution empirique".

Il est commode d'effectuer un "groupage en classes".

On divise l'intervalle dans lequel varie le caractère étudié en classes et on groupe ensemble les valeurs observées tombant dans la même classe. Nous avons donc des "frontières de classes" et une "valeur centrale" pour chaque classe.

Un tableau tel que le tableau I peut être dressé, où nous avons porté à la fois les *effectifs* par classe et également la *fréquence:* $f_i : \frac{n_i}{N}$

f_i = fréquence dans la classe i
n_i = effectif de la classe i
N = nombre total d'observations.

2.2—REPRESENTATION GRAPHIQUE DES DISTRIBUTIONS.

2.2.1—HISTOGRAMME.

On porte en abscisse les frontières de classe et en ordonnée les effectifs ou, mieux, la fréquence.

On construit ainsi une succession de rectangles accolés appelée histogramme.

2.2.2—COURBE DE FRÉQUENCE

La courbe de fréquence vient d'un "polissage" de l'histogramme.

Le concept de courbe de fréquence d'une série statistique est de la plus haute importance.

Celle-ci est considérée comme la représentation géométrique d'une loi idéale de distribution du caractère étudié.

2.3—DESCRIPTION DES DISTRIBUTIONS STATISTIQUES.

Les distributions ainsi obtenues se présentent sous forme de tableaux numériques comprenant un grand nombre de chiffres.

Il s'agit de synthétiser ces résultats avec un petit nombre de paramètres permettant de dégager les traits principaux.

2.3.1—CARACTÉRISTIQUES DE TENDANCE CENTRALE

2.3.1.1—Le mode.

C'est la valeur du caractère correspondant au plus grand nombre d'observations.

2.3.1.2—La médiane.

La médiane est la valeur du caractère autour de laquelle se partagent par moitié les valeurs observées.

2.3.1.4—La moyenne géométrique.

La moyenne géométrique de n données est la racine ième de leur produit.

Le logarithme de la moyenne géométrique de plusieurs données est la moyenne arithmétique des logarithmes de ces données.

Lorsque une série de données présente une grande dissymétrie, la moyenne géométrique est plus utile que la moyenne arithmétique.

2.3.2—LES CARACTERISTIQUES DE DISPERSION.

2.3.2.1—L'écart moyen.

$$é = \Sigma_i \; n_i \; \frac{|x'_i - m'_i|}{N}$$

On forme pour chaque observation la différence en valeur absolue entre sa valeur et la moyenne de la distribution, puis on divise la somme des différences obtenues par le nombre total d'observations.

C'est une valeur difficile à manier et peu utilisée.

2.3.2.2—La variance et l'écart type.

On remplace dans la formule précédente les $|x'_i - m'_i|$ par leurs carrés.

$$\sigma^2 = \Sigma_i \; \frac{n_i \, |x'_i - m'_i|^2}{N}$$

σ est l'écart type. C'est l'indice le plus utilisé.

3.—AJUSTEMENT D'UNE COURBE À DES DONNÉES

Nous n'entrerons pas dans le détail; disons seulement que l'examen de la courbe de fréquence suggère des "permanences statistiques" apparaissant dans des phénomènes les plus divers.

Ceci conduit à penser que le caractère étudié s'ajuste à une "loi statistique".

Parmi ces lois, deux sont particulièrement importantes.

3.1—LOI NORMALE,

ou loi de Gauss-Laplace, ou courbe en cloche, c'est la loi la plus connue mais ce serait une erreur de croire que c'est la seule loi du hasard. C'est la loi que l'on obtient lorsque les causes initiales jouent de manière indépendante en s'ajoutant.

3.2—LOI LOGNORMALE,

ou loi logarithmo-normale. C'est une généralisation de la loi normale où l'on a fait un changement de variable. La loi redevient normale en partant des logarithmes du caractère en abscisse.

Cette loi est générale lorsque les causes initiales indépendantes agissent de manière multiplicative.

Cette loi est probablement plus répandue que la loi normale. Elle est en fait l'expression de la loi d'action de masse.

Signalons que:

— le revenu des individus composant une nation,
— la taille des grains dans les échantillons de roches sédimentaires,
— la taille des grains d'argent dans une émulsion photographique,
— la sensibilité des animaux d'une même espèces aux produits chimiques,
— la quantité d'électricité utilisée aux U.S.A. dans les maisons de classes moyennes,
— les teneurs en or dans les mines du Rand,
— les teneurs des métaux dans une roche,
— le nombre de mots dans les phrases de l'oeuvre de G. B. Shaw,
— la dispersion du tir des mortiers,

suivent une loi lognormale.

Souvent une loi paraît normale lorsque l'imprécision des mesures est du même ordre que l'amplitude du phénomène de dispersion étudié.

3.3—TEST DE LA DROITE DE HENRY.

C'est un moyen commode de vérifier si une distribution peut, ou non, être assimilée à une loi normale ou lognormale.

On utilise des tables ou mieux du papier spécial, dit gausso-logarithmique ou gausso-arithmétique.

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THE BEHAVIOR OF SELENIUM IN THE ZONE OF OXIDATION *

H. W. LAKIN and A. R. TRITES, JR. * *

ABSTRACT

The selenium released during the oxidation of seleniferous sulfide minerals is in a less mobile form than the sulfur, and tends to be concentrated in the oxidized zone. Studies of some of the seleniferous pyrite-bearing sandstone type uranium deposits in Wyoming have shown that secondary selenium minerals are concentrated either in mantles overlying the unoxidized ore bodies, or in haloes enclosing these bodies. The highest grade seleniferous rock in the oxidized zone is commonly sandstone containing red elemental selenium with varying amounts of hydrous iron oxide that is believed to contain basic ferric selenite. In contrast sulfate-sulfur occurs in abundant quantities in gypsum and jarosite.

The separation of sulfur and selenium in the zone of oxidation can be explained by the differences in the oxidation potentials for the various reactions of these elements. The magnitude of the oxidation potential (—0.17 v) of sulfur to sulfate is such that moist air readily oxidizes sulfur to sulfate, whereas the magnitude of the potential of selenium to selenite (—1.15 v) is such that the reaction proceeds very slowly, if at all.

INTRODUCTION

Studies of seleniferous pyrite-bearing sandstone-type uranium deposits in the Gas Hills and Baggs areas, Wyoming, have shown that red elemental selenium is concentrated either in a discontinuous mantle overlying the unoxidized ore or in haloes enclosing the bodies. These haloes impart a violet-pink color to the weathered uncemented sandstones adjacent to seleniferous pyritic lenses and contain as much as 2.4 percent selenium. Selenium is also enriched in gossans of former pyrite lenses, and held as basic ferric selenites. In contrast sulfur is oxidized to sulfate as shown by the abundance of gypsum and jarosite in the oxidized zone. Small quantities of selenium are found with the sulfates. These observations on the behavior of selenium, as compared to sulfur, in the zone of oxidation in the Wyoming deposits are amenable to explanation as a function of the oxidation potentials of the various reactions of these two elements.

A distinctive, penetrating, garlic-like odor is evident when the seleniferous pyritic uranium ore is exposed by mining operations, and persons studying

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* *Publication authorized by the Director, U. S. Geological Survey.*

* * *U. S. Geological Survey.*

these deposits have ascribed the odor to selenium but without verification. Experimental evidence that the selenium is present in a volatile form in the ore has been obtained but the composition is unknown.

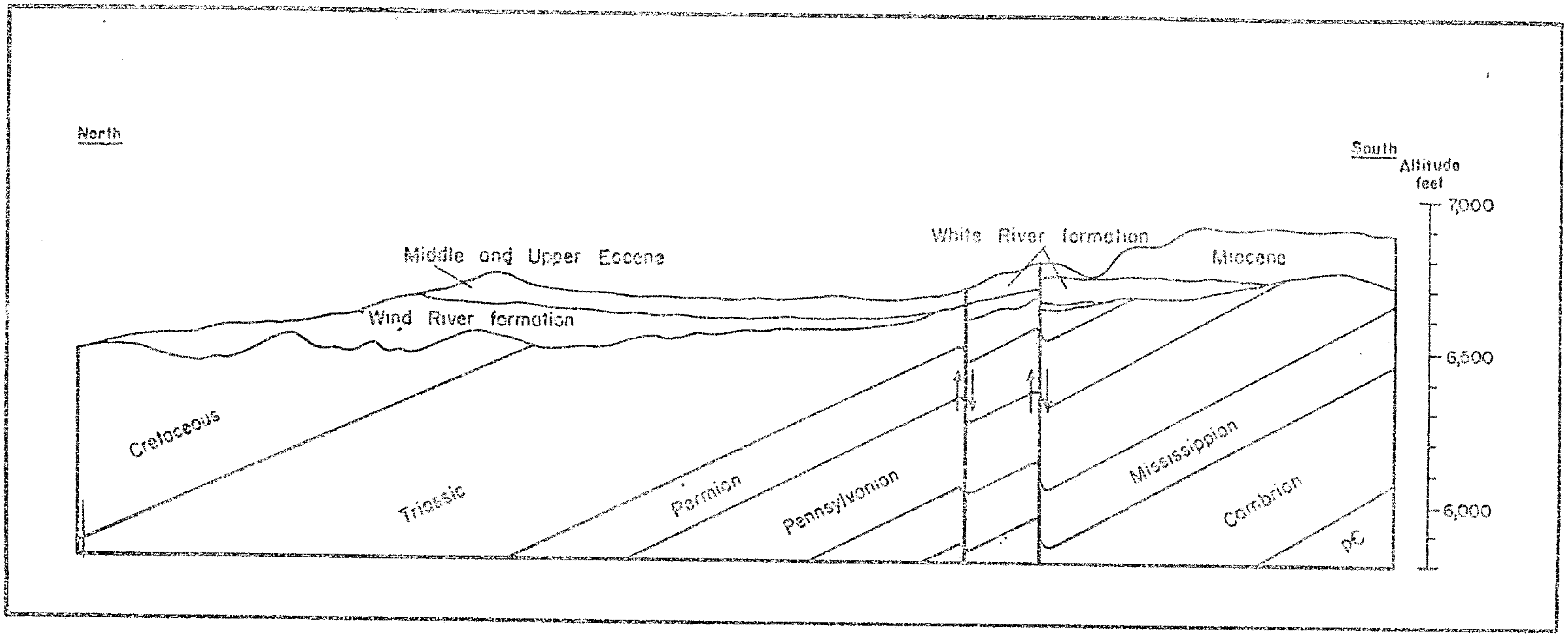
LOCATION OF OXIDIZED SELENIUM DEPOSITS IN THE WESTERN UNITED STATES

Two areas in Wyoming, the Gas Hills area in the central part and the Baggs area on the Wyoming-Colorado border, contain seleniferous pyritic sandstone-type uranium deposits that illustrate the oxidation pattern of selenium. Similar patterns of selenium oxidation can be seen in the uranium deposits of the Colorado Plateau, but the relationships of these deposits to the water table are not as evident.

GAS HILLS AREA:

The uranium deposits in the Gas Hills area are in the coarse-grained upper part of the Wind River formation of early Eocene age. The relationship of the Wind River to the other formations in the area is shown in Figure 1. The upper part of the Wind River formation is composed primarily of coarse-grained arkosic sandstone, conglomerate, siltstone, and shale. Uraninite, coffinite, and pyrite are disseminated in interbedded siltstone and sandstone about 50 feet below the surface and in lenses of calcareous sandstone scattered throughout the overlying beds. The main siltstone-sandstone ore body ranges from 5 to 20 feet in thickness; the top of this ore body is nearly coincident with the water table. Some of the uraniferous lenses in the oxidized zone above the water table contain material of ore grade; these lenses are as much as 100 feet across and 3 feet thick. Many of the uraniferous lenses have been partially oxidized and contain secondary uranium minerals, jarosite, iron oxides, and ilsemannite, in addition to the uraninite, coffinite, and pyrite. The sandstone beds enclosing the uraniferous lenses contain iron oxides, jarosite, gypsum, and secondary uranium phosphates, silicates, and carbonates. A diagramatic cross-section of the general distribution of selenium in the selenium deposits is shown in Figure 2.

Although selenium is disseminated through most of the upper part of the Wind River formation, it is most highly concentrated in some of the pyrite bearing uraniferous sandstone lenses, at or slightly below the water table, and in 1 to 3 feet wide, violet-pink haloes surrounding some of these lenses in the oxidized zone. These haloes and sandstone lenses contain from 0.1 to 2.7 percent selenium. The second greatest concentrations, 0.01 to 0.1 percent selenium,



Geology by H. D. Zeller

FIGURE I.- DIAGRAMMATIC CROSS-SECTION SHOWING RELATIONSHIP OF WIND RIVER FORMATION TO OTHER ROCKS are found in a discontinuous mantle, slightly less than a foot thick, at the water table; in some of the pyrite-bearing sandstone lenses of the oxidized zone; and in local concentrations of iron oxides in the oxidized zone. The third greatest concentration of selenium, 0.001 to 0.01 percent, occurs in most of the enclosing sandstones and siltstone above the water table.

The selenium in the pyrite-bearing sandstone, both above and below the water table is contained in pyrite and possibly in small quantities of marcasite. Robert Coleman (1956) of the U. S. Geological Survey has found as much as 1.4 percent selenium in pyrite concentrates. The selenium seems to be most highly concentrated in pyrite in lenses above to slightly below the water table. A single sample of a pyrite-bearing lens at about six feet below the water table contained only 0.001 percent selenium, suggesting that the selenium content of the pyrite is small in the sandstone at depths below the water table; the pyrite in the interbedded siltstone contains insignificant amounts of selenium.

Red elemental selenium imparts a violet-pink color to the haloes surround-

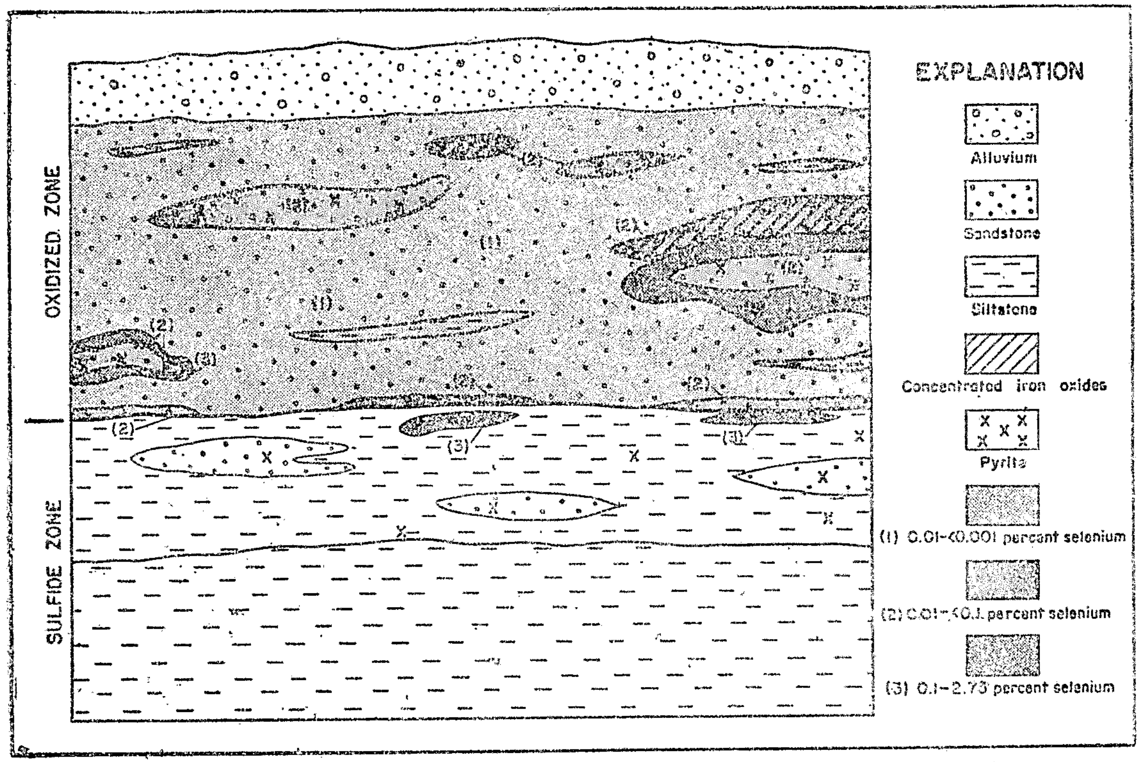


FIGURE 2.-DIAGRAMMATIC CROSS-SECTION SKETCH OF THE DISTRIBUTION OF SELENIUM IN THE URANIUM DEPOSITS OF THE GAS HILLS AREA, FREMONT COUNTY, WYOMING

20 0 20 40 Feet

Horizontal equals vertical scale

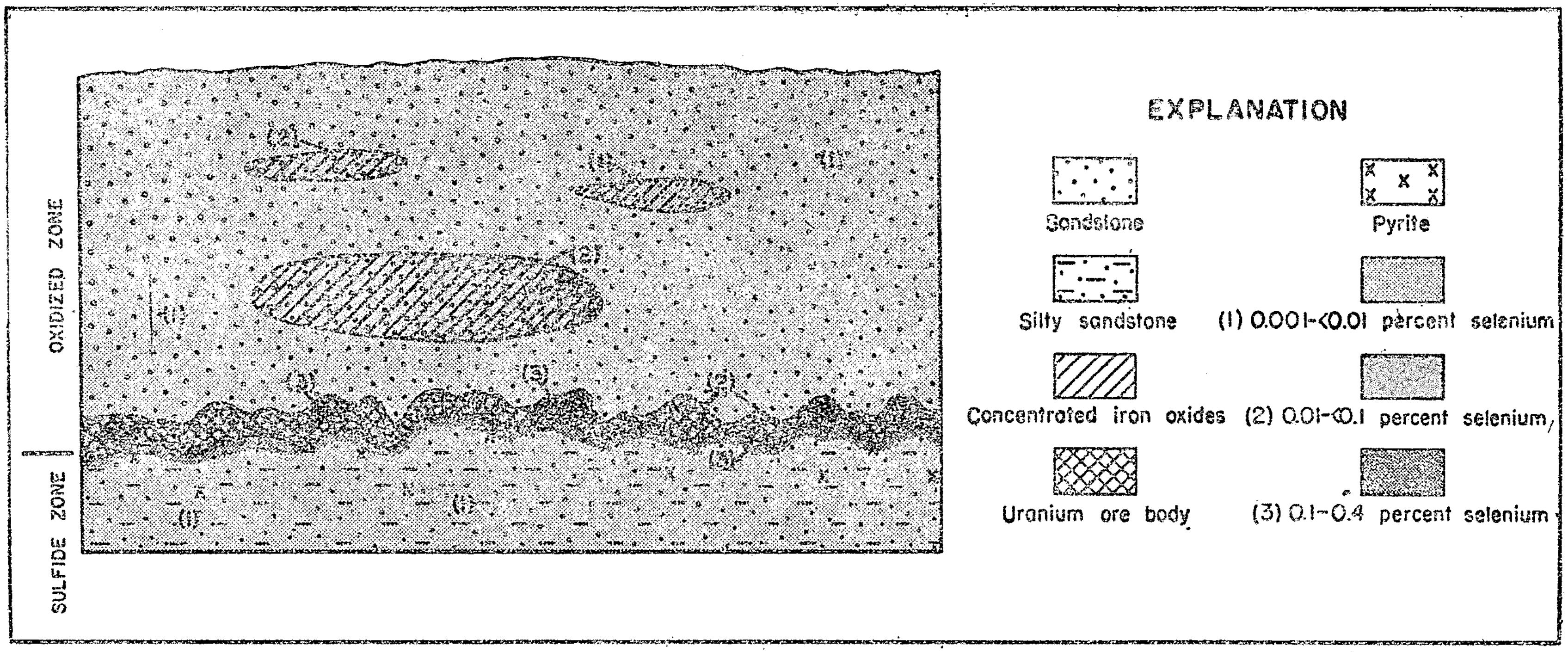


FIGURE 3.-DIAGRAMMATIC CROSS-SECTION SKETCH OF THE DISTRIBUTION OF SELENIUM IN THE URANIUM DEPOSITS OF THE BAGGS AREA, CARBON COUNTY, WYOMING

20 0 20 40 Feet

Horizontal equals vertical scale

ing the pyrite-bearing sandstone lenses in the oxidized zone and in the thin zone mantling the water table. Some of the selenium contained in the concentrations of iron oxides is believed to be in the form of basic ferric selenite. Areas in the oxidized zone that contain abundant sulfates, such as gypsum and jarosite, contain only small quantities of selenium, suggesting the separation of sulfur and selenium by oxidation of the pyrite and redistribution in the zone of oxidation.

BAGGS AREA:

Somewhat analogous occurences of selenium have been found in the sandstone-type uranium deposits in Poison Basin, near Baggs, Wyoming. Here the seleniferous uranium deposits are in sandstone of the Browns Park formation of Miocene age. A diagramatic cross-section of the distribution of the selenium is shown in Figure 3. The contact between the pyritic zone and the overlying oxidized zone may represent a fossil water table.

Selenium occurs in the main oxidized ore horizon in the underlying gray pyrite-bearing beds, and in the overlying limonitic sandstone. The highest concentration, 0.1 to 0.4 percent selenium, is contained in pyritic sandstone in the uppermost part of the unoxidized zone and in small lenses of disseminated red elemental selenium in the uranium ore zone. Intermediate concentrations, 0.01 to 0.1 percent, are contained in the ore body and in some lenses and irregular masses of iron oxide in the oxidized zone. Lower grade selenium concentrations, 0.001 to 0.01 percent, occur generally throughout the oxidized zone and in the pyrite-bearing sandstone and siltstone below the unoxidized ore.

COLORADO PLATEAU:

Selenium is known to occur in the uranium deposits of at least ten areas of the Colorado Plateau where native selenium, selenium-bearing pyrite and marcasite, and clausthalite, the lead selenide have been identified. The deposits of the Temple Mountain and the Henry Mountain areas seem to contain the highest grade seleniferous rock. The general observations of the selenium in the uranium deposits previously discussed appear to hold for the occurrence in the Colorado Plateau except that the red elemental form occurs more in an envelope surrounding the uraniferous deposits, and the relationships of the water table to the deposits are less evident.

COMPARISON OF OXIDATION POTENTIALS OF SELENIUM AND SULFUR

In an oxygen-deficient environment selenium is associated with sulfur; it is found enriched in magmatic sulfides and volcanic sulfur. However, in the zone of oxidation the greater affinity of sulfur for oxygen results in the separation of these elements. A study of the oxidation potentials of various reactions for selenium and sulfur (see table 1) clarifies the behavior of selenium and sulfur in the zone of oxidation.

The oxidation potentials of selenium for various reactions in 1. N acidic and 1. N basic solutions are given in the second and 4th columns of table 1. Columns 3 and 5 show the oxidation potentials for analogous reactions of sulfur. These oxidation potentials are those given by Latimer (1952) and follow his sign convention.

A study of these oxidation potentials reveals some striking differences between the two elements. The oxidation potentials lead one to expect that hydrogen sulfide would be stable in aqueous solutions, whereas hydrogen selenide would reduce water to give hydrogen gas. Actually, due to overvoltage effects and in the absence of air, aqueous solutions of hydrogen selenide can be prepared. Hydrogen selenide, similarly to hydrogen sulfide, can be prepared by adding hydrochloric acid to a ferrous selenide but the gas, unlike hydrogen sulfide, decomposes in the moist air above the acid.

TABLE 1

COMPARISON OF OXIDATION POTENTIALS OF VARIOUS REACTIONS OF SELENIUM AND SULFUR

Reaction	1 N acid		1 N base	
	Se volts	S volts	Se volts	S volts
$H_2X^* \rightarrow X^\circ + 2H^+ + 2e^-$	+0.40	—0.14		
$X + 3H_2O \rightarrow H_2XO_3 + 4H^+ + 4e^-$	—0.74	—0.45		
$H_2XO_3 + H_2O \rightarrow XO_4^{--} + 4H^+ + 2e^-$	—1.15	—0.17		
$X^{--} — X^\circ \rightarrow 2e^-$			+0.92	
$X^\circ + 60H^- \rightarrow XO_3^{--} + 3H_2O + 4e^-$			+0.37	+0.66
$XO_3^{--} + 20H^- \rightarrow XO_4^{--} + H_2O + 2e^-$			—0.05	+0.93

* = Se or S.

Although hydrogen selenide is much more easily oxidized to selenium than hydrogen sulfide to sulfur, a comparison of the oxidation potentials for the oxidation of selenium to selenium dioxide (E = —0.74 volts) and sulfur to sulfur dioxide (E = —0.45 volts) shows that sulfur is more casily oxidized than selenium to the dioxide. The quantitative reduction of selenous acid by sulfurous acid in dilute hydrochloride acid solutions is illustrative of this difference.

The difference between the oxidation potentials for selenous acid to selenic and sulfurous to sulfuric acid is even more pronounced. Sulfur is oxidized slowly by moist air to sulfuric acid; whereas, selenium is oxidized less easily to selenium diaxide, and hot concentrated nitric acid is not a sufficiently strong oxidizing agent to oxidize selenium to selenic acid.

BEHAVIOR OF SELENIUM IN THE OXIDATION OF PYRITE IN WYOMING

HALOES OF RED ELEMENTAL SELENIUM:

The oxidation of pyrite by moist air results in the production of dilute sulfuric acid and the evolution of heat. In this environment the selenide-selenium in the pyrite may be released as hydrogen selenide, oxidized to elemental selenium, or even to selenium dioxide. In the absence of a continuous aqueous phase, hydrogen selenide may be evolved and travel short distances before being oxidized by moist air to selenium and water. This behavior is more likely in an open structure, such as exists in the weathered uncemented sandstones at Gas Hills and Baggs, Wyoming. A sample of pyritic sandstone from the Gas Hills area was heated with dilute sulfuric acid and the evolved gases passed through a sodium hydroxide solution. Thirty micrograms of selenium were found in the alkaline solution. Neither selenium nor selenium dioxide are volatile under the conditions of this experiment. In another experiment a sample of ferrous selenide was placed in a flask connected to a train containing moist glass beads and finally a water trap, dilute hydrochloric acid was added and the flask warmed. Red elemental selenium precipitated on the sides of the flask, coated the connecting tubes of the train, imparted a pink color to the glass beads, and finally formed a pink precipitate which colored the water in the trap. In addition to these observed facts, the oxidation potentials indicate that hydrogen selenide would be easily oxidized to selenium but relatively difficult to oxidize to selenium dioxide. One may conclude that the red elemental selenium observed in the Gas Hills and other areas is the result of the evolution of hydrogen selenide during the oxidation of pyrite and its subsequent oxidation by moist air to selenium and water.

VOLATILE SELENIUM:

The distinctive penetrating garlic-like odor observed when seleniferous pyritic uranium ore is exposed by mining operations is due to a selenium compound of unknown composition. In an experiment to determine the possible presence of selenium in the volatile substance, 4 kilograms of this odoriferous ore was placed in a desiccator and moist air passed slowly through the desiccator into a hydrobromic acid-bromine trap for a period of 3 weeks; 22 micrograms of selenium were found in the trap. The odor is not evident in the moist pink seleniferous sandstones containing one percent selenium, but is distinctly evident in a moist light gray pyritic sandstone containing only 0.025 percent selenium. This odor does not closely resemble the odor of hydrogen selenide but is similar to that obtained by slowly bubbling air through a suspension of ferrous selenide in water. According to Mellor (1930) J. J. Berzelius stated that sulfur will reduce selenious acid in acid solution to selenium monoxide. He described selenium monoxide as a colorless gas with an odor like that of horse-radish, and so strong that one-fiftieth of a grain is sufficient to fill a room with its odor. Several chemists have attempted to repeat Berzelius' experiments and finally V. Lenher concluded that selenium monoxide does not exist. The material Berzelius described as selenium monoxide fits the description given to the odors encountered in the Wyoming selenium rich sandstones. One cannot, with the information available, deny the possibility of the existence of selenium monoxide in these deposits. The odoriferous gas given off by the ores at Gas Hills and Baggs, Wyoming may be selenium monoxide, hydrogen selenide, or an organic selenide, but most certainly, it contains selenium.

SELENIUM IN IRON OXIDES:

Selenium is oxidized by moist air to selenious acid. Very dilute solutions of its salts will react with ferric chloride to form an extremely insoluble precipitate whose composition is approximately that of basic ferric selenite, $Fe_3(OH)_4SeO_3$ (Williams and Byers 1936). These authors report that the selenite ion can be removed from solution by shaking over night with a ferruginous soil; selenates are not quantitatively removed by the same treatment. Further evidence of the stability of the complex iron selenite is the report that ferruginous soils of Hawaii under an annual rainfall of 100 inches contain 20 to 26 ppm of selenium (Byers and others, 1936). It is therefore reasonable to assume that the selenium in the concentrated iron oxide lenses at Gas Hills is held as a complex iron selenite.

SELENIUM IN GYPSUM AND JAROSITE:

The lack of a measurable quantity of selenium in the gypsum and jarosite at Gas Hills is readily explained by the extremely high oxidation potential for the formation of selenate ions, but the reported occurrence of selenates in the zone of oxidation requires more careful consideration, Williams and Byers (1936) demonstrated the presence of minute quantities of selenates, probably calcium selenate, in the soils of South Dakota. Olson and others (1942) state that during weathering of seleniferous rock to soil in South Dakota a large part of the selenium is oxidized to the selenate form. Beath and others (1946) report the occurrence of selenates in various localities in Utah and Wyoming and essentially all of the selenium (173 ppm out of a total of 187 ppm) occurred as selenate in volcanic tuffs of Tertiary age in Fremont County, Wyoming. These tuffs overlie the Wind River formation in the Gas Hills area.

Delahay and others (1952) published an equilibrium diagram showing the variation of oxidation potential with pH for the various ionic species of selenium. According to this data at a pH of 7.5 the oxidation potential for the couple $SeO_3^{=}$ —$SeO_4^{=}$ is —0.4 volts and for H_2O — O_2 is —0.77 volts. On the basis of these oxidation potentials it is possible for moist air to oxidize the selenite to selenate in slightly basic solutions; the selenate ion, once formed, is very stable, thus favoring the reaction. Selenates are not reduced by hydrogen sulfide, sulfur dioxide, or ferrous iron, all of which reduce the selenite to selenium. The evidence of the existence of the selenate form of selenium in Wyoming is sufficient to warrant the statement that selenites are oxidized to selenates in the zone of oxidation. The reaction probably is accomplished by moist air in slightly alkaline solutions. Lipman and Waksman (1923) described a bacterium capable of oxidizing elemental selenium to selenic acid; this provides another possible mechanism for the formation of selenates.

BEHAVIOR OF SELENIUM IN THE ZONE OF REDUCTION

The seleniferous pyrite overlain by a mantle of red selenium near a fossil water table in the Baggs area, Wyoming may be the result of enrichment by downward leaching of selenites and subsequent reduction to elemental selenium and selenides. Under sufficiently reducing conditions selenides are formed and the ionic radii of the selenide ion (1.91) and sulfide ion (1.74) are sufficiently alike to permit the replacement of sulfur by selenium in pyrite. Thus the selenium rich pyrites may be formed by downward leaching of selenium from oxidized bodies above the ore and subsequent reduction below the water table.

The observed pattern at the fossil water table in Baggs is also explained by the simple oxidation of the seleniferous pyrite but such explanation does not account for the presence of the seleniferous pyrite in a narrow band just below the water table.

CONCLUSIONS

This study of the behavior of selenium in the zone of oxidation observed in Wyoming permits some observations regarding the general behavior of selenium: In an oxygen defficient environment selenium is associated with sulfur; it is found enriched in magmatic sulfides and volcanic sulfur. However, in the zone of oxidation the greater affinity of sulfur for oxygen results in the separation of these elements. Sulfides are readily oxidized to sulfates and travel long distances in the ground waters and streams; selenides are readily oxidized to elemental selenium and eventually oxidized to selenites. These form insoluble complex iron salts and are concentrated in hydrolyzates. In this respect selenium behaves like arsenic.

In the semiarid regions of the western United States appreciable quantities of selenium are oxidized to the selenate form. The selenates resemble the sulfates in stability and solubility. Once formed, they may move great distances in the ground and surface waters as shown by the presence of selenium in the water of wells, springs, and streams in the Western United States.

Finally, we may assume that small amounts of selenium are being removed from seleniferous sulfide deposits by surface and underground waters and is eventually discharged into the ocean and inland basins, some is locally retained in the rock and soil by precipitation as basic ferric selenite, some may be leached downward are reduced to selenides, some is retained temporarily by absorption in certain plants, and a small amount enters the atmosphere as a gas.

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MOVEMENT OF METALLIC ELEMENTS IN SHALLOW COLLUVIUM *

F. B. Lotspeich * *

ABSTRACT

As part of an investigation of the effects of the biogeochemical environment on the movement of various elements in the zone of weathering, trenches were cut through colluvium and into the phosphate beds of the Phosphoria formation, which is known to contain several metals in greater than normal amounts for sedimentary rocks. Somples of the phosphate beds and the colluvial soils were collected and analyzed for Cr, Cu, Ni, P, V, and Zn by colorimetric or spectographic methods, or both. These analyses provide data to evaluate the degree of enrichment of the colluvium with metals from the underlying phosphate beds by biological, chemical, and physical processes.

Various elements behave differently: copper and nickel tend to be immobile, whereas zinc and phosphorous tend to move into the colluvial soil. Vanadium tends to become concentrated in the upper humus layer; in contrast, zinc in this layer is at a minimum and gradually increases with depth, reflecting its high mobility in the near-surface environment. Chromium behaves similarly to vanadium.

INTRODUCTION

The behavior of metallic elements in the zone of weathering is controlled by environmental conditions such as climate, plant assemblages, soil chemistry, and character of the parent rock. These affect strongly the potential of geochemical methods for mineral exploration. The inter-relationships of plant cover and soil to the underlying substratum is of the utmost importance. This investigation is an attempt to obtain answers to the following three questions:

1—How do dry and moist climates affect the metal content of a soil?

2—What mechanisms operate to enrich a barren colluvial soil over a metal-rich substratum?

3—What is the minimum quantity of a particular metal in the substratum that will yield enough in the overlying soil to be significant in geochemical exploration?

The Phosphoria formation of Permian age near Montpelier in southeastern Idaho appears to be well suited to such an investigation for four reasons: First,

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* *Publication authorized by the Director, U. S. Geological Survey.*

* * *U. S. Geological Survey.*

the Phosphoria formation contains several metals in appreciable quantity; second, the beds are remarkably persistent and uniform in chemical composition for tens of miles; third, a climatic range from semiarid to subhumid is available; fourth, many outcrops are covered with a metal-deficient colluvium not derived from the Phosphoria formation.

To evaluate the effects of climatic differences on the metal content of the soil, two sites were chosen in the Montpelier area where the Phosphoria formation attains its maximum thickness. The Dingle site is about 20 miles south of Montpelier, Idaho, in a semiarid location where annual mean precipitation is about 15 inches. The East Georgetown site is on the western slope of Snowdrift Mountain 20 miles north of Montpelier in a subhumid location where the mean annual precipitation is 23 inches (Fig. 1). At the Dingle site, 6,200 feet above sea level, the temperature ranges from -34°F to 102°F, and at the East Georgetown site, 8,300 feet above sea level, the temperature averages 6° cooler.

The Phosphoria formation in southeastern Idaho has two members: the Rex chert member, or upper one, about 250 feet thick; and the lower one, the phosphatic shale member, consisting of about 180 feet of phosphate rock, mudstone, and massive carbonate rock (Fig. 2). The Phosphoria formation is underlain by the Wells formation of Pennsylvanian age, a series of limestones, dolomites, and sandstones more than 5,000 feet thick. The Phosphoria formation is overlain by the Dinwoody formation of Triassic age at the East Georgetown site and by the Tertiary Wasatch formation at the Dingle site.

Snowdrift Mountain is near the axis of an anticline, and the outcrop of the phosphatic shale member of the Phosphoria sampled in this study lies on the western limb. The beds strike N 10° E. and dip 70° to the west. Although the general topography is mountainous with steep slopes, the land surface of the phosphatic shale member slopes only 10° westward, and on the Wells formation only about 25° westward. The land surface on the phosphatic shales slopes eastward at 10°, and on the Wasatch formation about 20° eastward.

The cooler, more moist environment at the East Georgetown site is reflected by an open mesophytic forest and shrubby vegetation. Aspen *(Populus tremuloides)* is the most conspicuous tree. Douglas fir *(Pseudotsuga taxifolia)*, Engelmann spruce *(Picea Engelmanni)*, lodgepole pine *(Pinus contorta)*, and subalpine fir *(Abies lasiocarpa)* are the most abundant conifers mixed with the aspen. The common shrubs are snowberry *(Symphoricarpus oreophilus)*, mountain mahogany *(Cercocarpus ledifolius)*, buckbrush *(Ceanothus velutinus)*, and mountain lover *(Pachistima myrsinites)*. In contrast, vegetation at the Dingle site is xerophytic. Overgrazing has seriously depleted the original grasses,

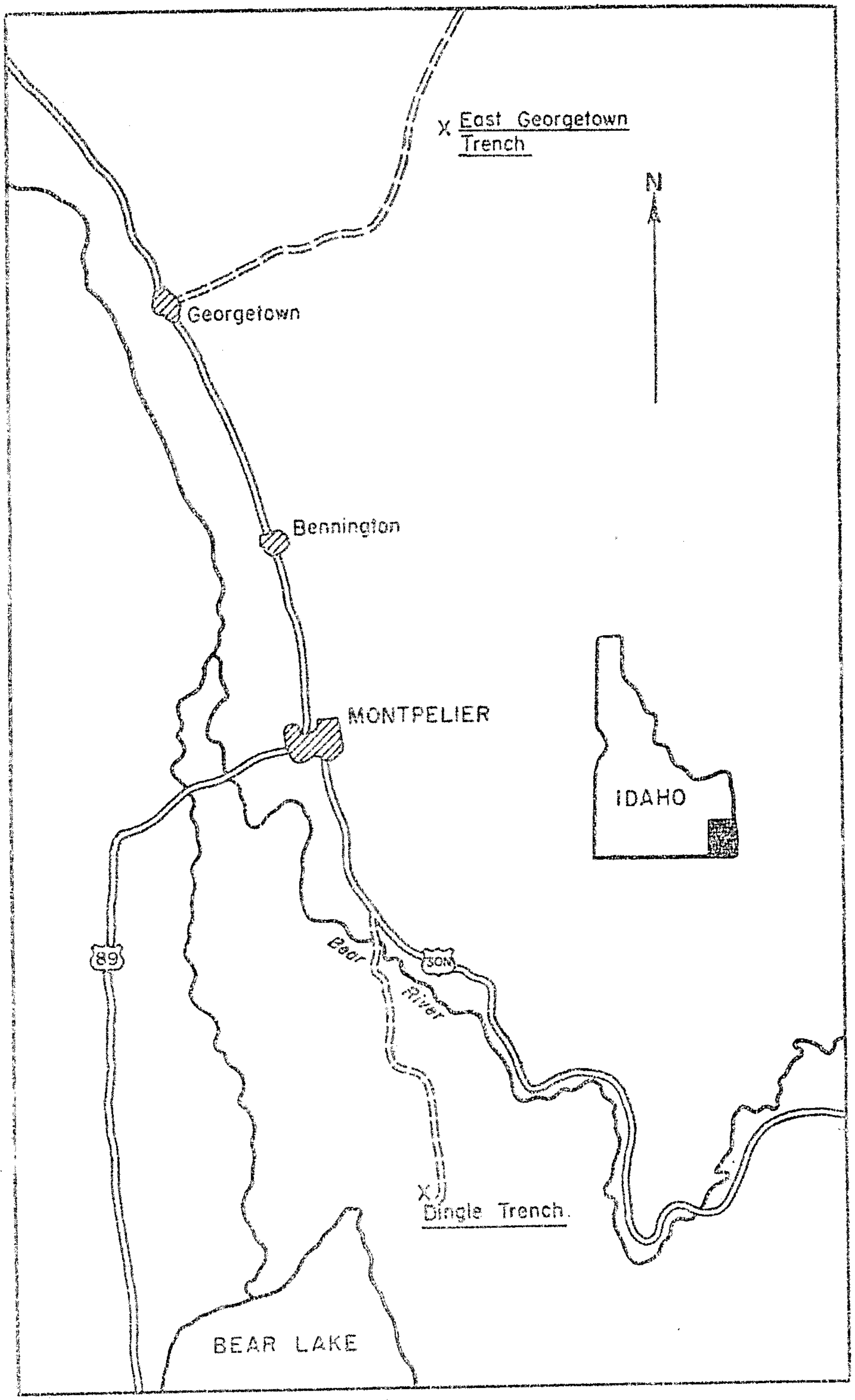
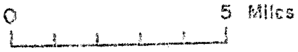


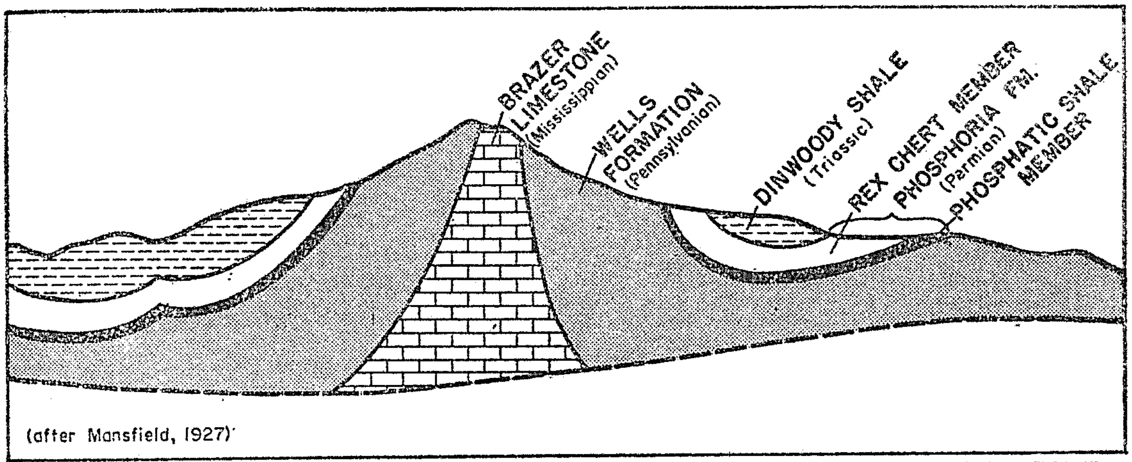
FIGURE I.-INDEX MAP SHOWING THE LOCATION OF THE DINGLE AND EAST GEORGETOWN TRENCHES, MONTPELIER, IDAHO



and shrubby species are now dominant. The chief shrubs are sagebrush *(Artemisia tridentata)* and rabbitbrush *(Chrysothamnus nauseosus)*.

EFFECT OF SEMIARID VERSUS SUBHUMID CLIMATES ON THE METAL CONTENT OF SOIL

To test the effects of a dry versus a moist climate on the metal content of colluvial soil, samples were analyzed for vanadium, chromium, copper, zinc, nickel, and phosphorus. The colluvium at the East Georgetown site originates from the Wells formation, whereas that at the Dingle site originates from the red Wasatch material. In the East Georgetown trench, the soil developed from the Wells formation and now overlying the Wells will be called the Wells residual soil, and the soil developed from the Wells formation and now overlying the Phosphoria, the Wells colluvial soil. Similarly for the Dingle trench, the soil developed from the Wasatch formation and now overlying the Wasatch will be called the Wasatch residual soil, and the soil developed from the Wasatch formation and now overlying the Phosphoria formation the Wasatch colluvial soil.



(after Mansfield, 1927)

FIGURE 2--GENERALIZED E-W CROSS SECTION OF SNOWDRIFT MOUNTAIN, EAST GEORGETOWN AREA, IDAHO

The main sampling emphasis was at the East Georgetown trench where samples of the phosphatic shale member and of the soils were collected (Figs. 2 and 3). Twenty-seven soil profiles were sampled in detail from the surface to the underlying phosphatic shale member. Sampling at the Dingle site was restricted to two soil profiles, one over the phosphatic shale member and one over the Wasatch residual soil. Samples of the phosphatic shale member were not collected at Dingle.

All samples were analyzed for minor elements by wet chemical or spectrographic methods. In addition to the minor elements, pH was determined on all soil samples, and selected soil samples were analyzed for exchangeable bases and exchange capacity. On 5 soil profiles the relative sand, silt, and clay content of the soil overlying the phosphatic shales was determined by particle size analysis.

Soil properties

The Wells colluvial soil has a pH of about 6.2 in contrast to 7.5 or higher for the Wasatch colluvial soil at the Dingle trench where the presence of free calcium carbonate at all depths below the surface was verified with acid. Although the Wells colluvial soil was derived from limestones and dolomites, it did not effervesce when acid was applied, this indicates a lack of calcium carbonate and reflects the more humid climate which caused leaching of free calcium carbonate from the profile. Base-exchange studies of the Wells colluvial soil show a high percent base saturation with the exchange complex dominated by calcium.

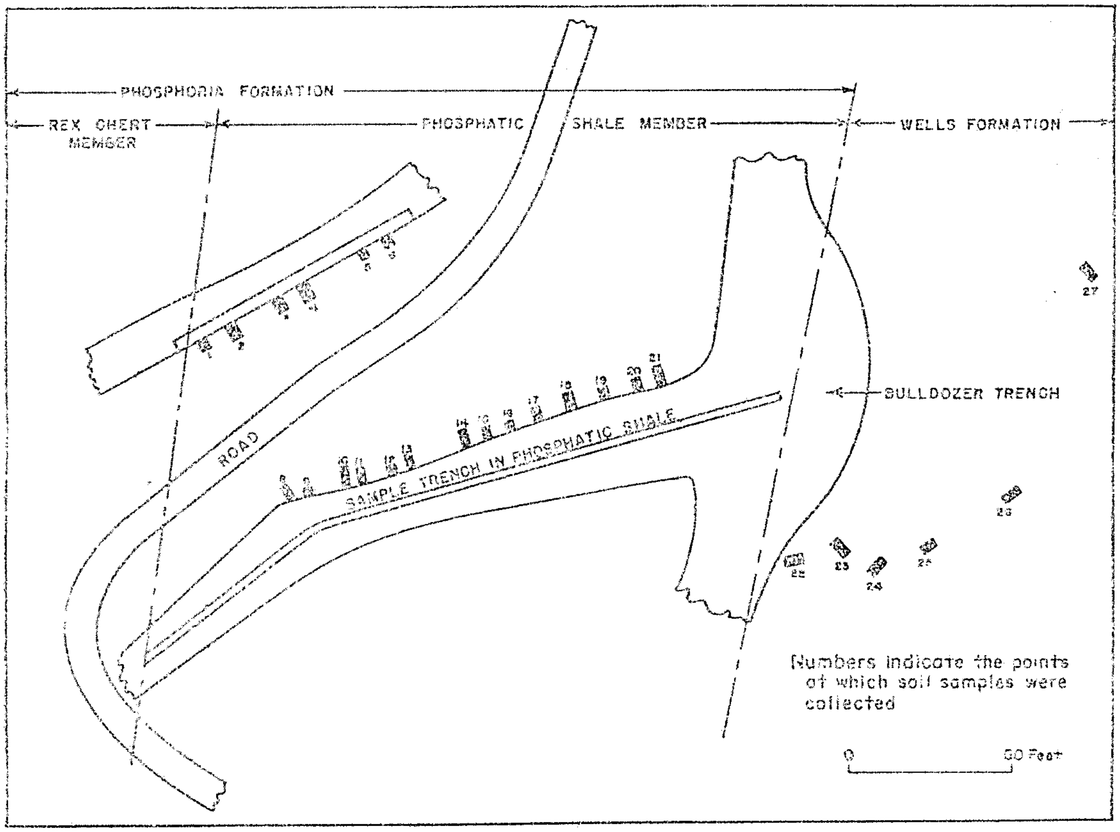


FIGURE 3 DETAILED MAP OF EAST GEORGETOWN TRENCH, SHOWING SAMPLING POINTS

The lack of horizon differentiation, the poor structure, and the high percent of base saturation indicate a low intensity of soil forming processes. The main soil forming process that has been operating at either site is that of calcification, which cycles calcium within the profile by plant processes and maintains a high degree of calcium saturation. The process of podzoliation (a soil-forming process that results in a bleached zone near the surface and the accumulation of iron and aluminum below this zone to give a red or brown color) is also probably operating under the present climatic regimen at the East Georgetown site.

METAL CONTENT OF PHOSPHORIA FORMATION

Some beds of the Phosphoria formation are low in phosphorus and may contain only 1,000 ppm; some of the higher grade beds contain 150,000 ppm of phosphorus (15 percent $P = 35$ percent P_2O_5). The vanadium and chromium content reaches a maximum of 5,000 ppm, but averages about 750 ppm V and 1,000 ppm Cr in the phosphatic shale member. There are two zones in which the vanadium content is high, one near the upper and one near the lower end of the section. The chromium content is restricted to definite beds, randomly scattered throughout the section. The zinc content has a maximum value of 3,500 ppm and a minimum value of 750 ppm in the phosphatic shale member. Although in most beds it does not exceed 100 ppm, the maximum cooper content is 500 ppm. Nickel never exceeds 350 ppm and most beds contain only a few ppm.

DESCRIPTION OF THE EAST GEORGETOWN SITE

The bulldozer trench at East Georgetown revealed some interesting surface geology (Fig. 4). Despite the relatively gentle surface slope of 10°, the phosphatic shale member is covered by colluvium, 1 1/2 to 4 feet deep that is derived from the Wells formation. A particle-size distribution study, which revealed a high sand content, and the presence of large limestone and dolomite fragments within the colluvium, eliminates the possibility that the colluvium was derived from the Phosphoria formation by weathering and slumping. Although the shale beds of the Phosphoria formation dip 70° to the west, they have been dragged and smeared downslope by the overlying colluvium. Some of these beds, however, retain their characteristic colors and may be traced for distances of 40 to 50 feet. Despite the transport of colluvium across the Phosphoria Formation, there has been little or no mixing of the Wells colluvium with the colluvial phosphate material except at the contact. None of the soil

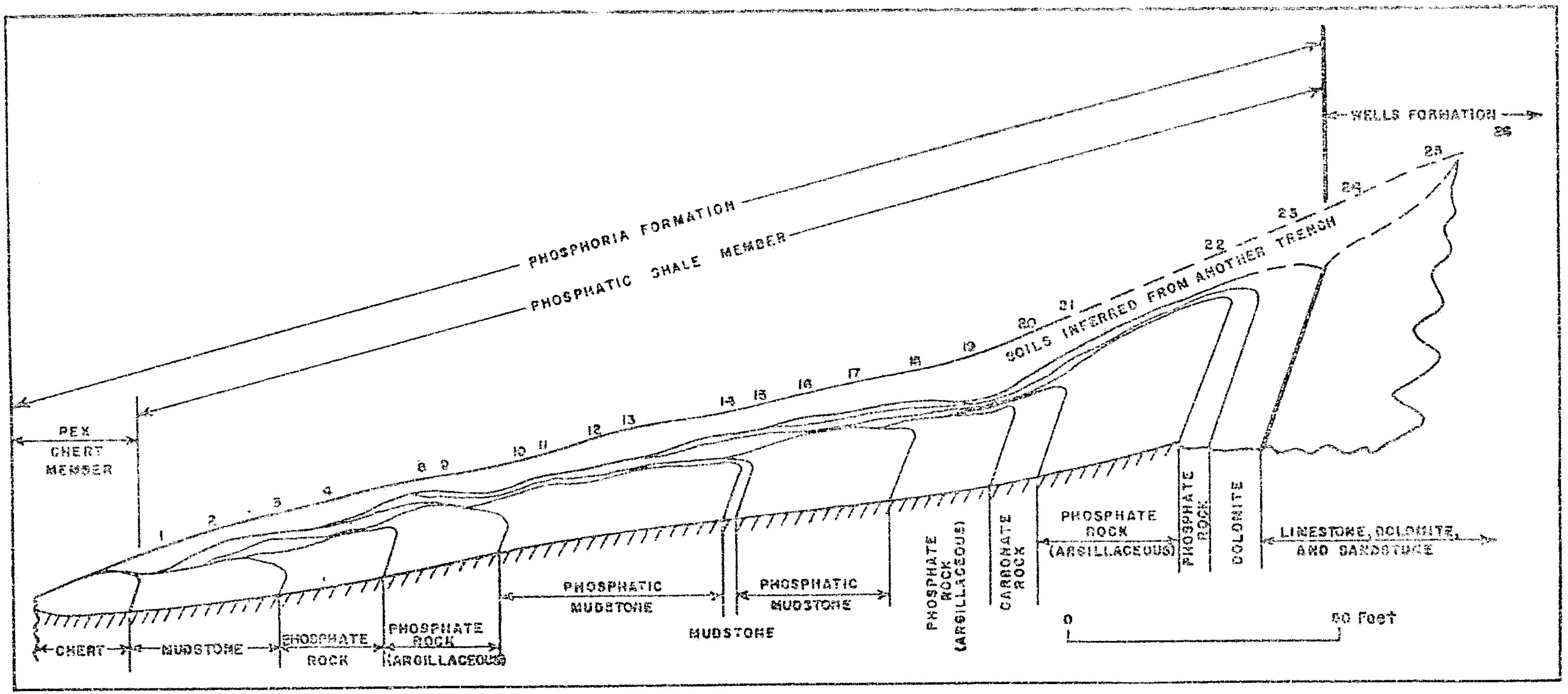


FIGURE 4. GENERALIZED DIAGRAM SHOWING SECTION OF THE EAST GEORGETOWN TRENCH, MAJOR GROUPS OF BEDS, AND POINTS AT WHICH SOIL PROFILES WERE SAMPLED

profiles contain phosphatic material above the contact of the Phosphoria and Wells colluvium.

The soil formed from the Wells colluvium at the trench is poorly developed as is shown by the weak structure and lack of distinct horizons. Addition of organic matter has caused some darkening of the upper 6 to 9 inches; otherwise, the soil is little different from the yellow-colored colluvium from which it has developed.

METAL CONTENT OF THE SOILS AT THE EAST GEORGETOWN SITE

Several interesting relationships become evident when the metal content for the three uppermost horizons of the collucial soil above the phosphatic shale member is compared with similar horizons of the residual soil at the East Georgetown trench (table 1). Copper concentrations in the Wells colluvial soil are actually less than for the Wells residual soil, 30 to 45 ppm compared to 50 to 75 ppm. The values for the Wells colluvial soil are the averages of 20 profiles along the trench, and although some horizons may contain as much as 150 ppm, most samples are of the order of 20 to 30 ppm. The Wells formation contains as much copper as this weakly developed soil, and even some of the colluvial phosphate contains 150 to 200 ppm copper and may be traced 40 to 50 feet downslope by its metal content. The copper content of the phosphate rock richest in copper is so low (150 to 200 ppm) that, when it is

TABLE 1

METAL CONTENT OF PHOSPHATE ROCK AND SOIL AT THE EAST GEORGETOWN TRENCH

MATERIAL		Cu ppm	Ni ppm	V ppm	Cr ppm	Zn ppm	P ppm
Phosphoria formation		500	350	5000	5000	3500	10,000$^+$
Wells colluvial soil horizons	0 – 6 in.	30	8	120	160	520	10,000
	6 – 12 in.	35	20	165	210	520	11,000
	12 – 16 in.	45	20	170	215	430	14,000
Wells residual soil horizons	0 – 6 in.	50	20	75	35	140	1,000
	6 – 15 in.	50	10	50	35	100	250
	15 – 23 in.	75	20	50	35	140	250

diluted by other phosphate beds lower in this metal, it is little different from ordinary soils; therefore, there has been no geochemically significant copper enrichment of the soil.

The nickel content is nearly identical, 8, 20, and 20 ppm nickel in the Wells colluvial soil compared to 20, 10, and 20 ppm in the barren Wells residual soil. Although the maximum nickel concentration in the phosphatic shale member is 350 ppm, it never exceeds 150 ppm in the colluvium from these shales immediately beneath the Wells colluvial soil. Under the conditions at East Georgetown, the overlying soil is not being significantly enriched with nickel. This may be because of the low concentration of nickel in the substratum or the effect of the high phosphate content on the mobility of nickel in the soil.

The vanadium content of the Wells colluvial soil is 2 to 3 times greater than the Wells residual soil, 120, 165, and 170 ppm compared to 75, 50, and 50 for the uppermost horizons. The soil above the phosphates is, therefore, being enriched with vanadium from the underlying vanadium-rich shales.

The behavior of chromium closely parallels that of vanadium, but its concentration is higher than vanadium in the Wells colluvial soil and lower than vanadium in the Wells residual soil. Concentrations of chromium are 160, 210, and 215 ppm in the colluvial soil, compared to 35 ppm in all horizons of the residual soil, a five-to sixfold increase in the colluvial soil.

Zinc concentration of the Wells colluvial soil is at least double that of vanadium and chromium, even though its maximum concentration in the phosphatic shale is 3,500 ppm. In comparing the soils it is evident that the Wells colluvial soil has three or four times the zinc content of the Wells residual soil, 525, 520, and 430 ppm as against 140, 100, and 140 ppm. This evidence strongly suggests that zinc is more mobile in the surface environment than are chromium vanadium.

Although phosphorus is not used in geochemical exploration, it behaves similarly to the metals already described. Thus, the phosphorus content for the upper three soil horizons of the Wells colluvium exceeds 10,000 ppm, whereas in the Wells residual soil it is 1,000 ppm in the surface horizon and decreases to 250 ppm in the deeper horizons (250 ppm of phosphorus is the amount to be expected in normal agricultural soils). This ten— to fortyfold increase in phosphorus concentration over the phosphatic shales must be due to enrichment from below.

In summary, the Wells colluvial soil is not being enriched with copper and nickel from the metal-rich Phosphoria formation at the East Georgetown site. On the other hand, chromium, vanadium, zinc, and phosphorus have been added to the Wells colluvial soil in significant quantities compared to those found in the Wells residual soils.

DESCRIPTION OF THE DINGLE SITE AND COMPARISON OF THE METAL CONTENT OF THE SOILS AT DINGLE AND EAST GEORGETOWN

The concentrations of certain metals in the soil at the Dingle site are somewhat different from those in the soil at East Georgetown (table 2). This may be expected when the soil properties and climates are considered: The soil at Dingle has a higher pH; there is less precipitation; and the entire profile is saturated with calcium carbonate. The Phosphoria formation at the Dingle site, however, is assumed to have a similar metal content as at the East Georgetown site.

Copper content of the Wasatch colluvial soil is nearly twice that of the Wells colluvial soil, although this increase may not be significant at these low concentrations — 75 ppm versus 45 ppm, respectively. The Wasatch residual soil and the Wells residual soil contain nearly identical quantities of copper. The nickel content of the soils at Dingle is not significantly greater than at the East Georgetown, although the residual Wasatch contains less nickel than the residual Wells — 20, 10, and 20 compared to 10, 10, and 5 ppm, respectively. The concentrations of vanadium and chromium in the Wasatch and Wells residual soils are closely similar. Vanadium is, however, about 5 times and chromium nearly 3 times as concentrated in the Wasatch colluvial soil as in the Wells colluvial soil; therefore, the degree of enrichment under the drier environment is more pronounced. Evidently under semiarid conditions, these metals are less mobile once they enter the soil than under subhumid.

TABLE 2

METAL CONTENT OF PHOSPHATE ROCK AND SOIL AT THE DINGLE TRENCH

MATERIAL		Cu ppm	Ni ppm	V ppm	Cr ppm	Zn ppm	P ppm
Phosphoria formation		500	350	5000	5000	3500	10,000+
Wasatch colluvial soil	0 – 2 in.	75	20	750	500	500	50,000
	2 – 6 in.	75	35	1000	500	625	100,000
	6 – 12 in.	50	20	750	500	500	50,000
Wasatch residual soil horizons	0 – 2 in.	50	10	75	35	75	3,000
	2 – 12 in.	50	10	75	35	75	1,000
	12 – 20 in.	35	5	50	35	75	1,000

Zinc concentration in the Wasatch colluvial soil is little different from similar horizons in the Wells colluvial soil, although the Wells residual soil is nearly twice as high in zinc as the corresponding Wasatch residual soil. The zinc content has been raised from 75 ppm in the Wasatch residual soil to 500 to 600 ppm in the Wasatch colluvial soil to give an enrichment factor of 6 or 7.

Phosphorus concentration of the soil overlying the phosphates is 5 to 10 times as high at Dingle as at East Georgetown. The higher phosphorus content of the Wasatch residual soil, compared to the Wells residual soil may be the direct result of the drier environment, or the Wasatch formation may contain more phosphorus than the Wells formation. The latter possibility was not investigated.

A comparison of the metal concentrations of the soils under a subhumid with a semiarid climate illustrattes that caution must be used in evaluating geochemical data from contrasting climatic environments. Thus, the colluvial soil under both climates is not being significantly enriched with copper and nickel from the underlying Phosphoria. However, under the semiarid climate, chromium, vanadium, zinc, and phosphorus are added to the colluvial soil in larger quantities than under a more subhumid climate.

MECHANISM OF ENRICHMENT

To evaluate the operative mechanisms of enrichment, the following must be considered: (1) the importance of mechanical mixing of the metal-deficiente colluvial material; and (2) the cause of a metallic gradient in the soil profiles, if one exists.

At the East Georgetown trench, portions of the phosphatic shale member beneath the Wells colluvial material are displaced for distances of 40 to 50 feet on a 10° slope without any observable mixing of these contrasting materials. The absence of such mixing prevents the metaliferous phosphates from enriching the relatively barren Wells residual colluvium by mechanical means. Therefore, the only way by which the colluvial soil could be enriched from beneath is by diffusion upward (capillarity) or by plant processes operating from the surface downward.

Detailed sampling and analysis of the colluvial soil and phosphatic shale at the East Georgetown site permits an evaluation of the probable mechanism of enrichment. These analyses should distinguish whether plant processes enrich the soil from the surface downward or if capillarity is enriching the soil from below. A gradient in metal content of the soil downward from the surface should suggest that plant processes are dominant, whereas a gradient upward from the bottom of the colluvium would indicate that capillarity is the process of enrichment.

DETAILED DESCRIPTION OF THE METAL CONTENT OF THE SOIL AT EAST GEORGETOWN

At the East Georgetown site, concentration of phosphorus in all the profiles over the phosphatic shale member is unusually high for mineral soils. Figure 5 compares the zinc and phosphorus content in the three top horizons of the Wells colluvium. Although most of the profiles contain less than 10,000 ppm phosphorus, three of them have up to 50,000 ppm of this element. All horizons of profiles No. 1 next to the chert, and No. 8, a very shallow profile approximately 50 feet from the Rex Chert member (the total depth of this soil is 12 inches) are high in phosphorus. Total phosphorus content of the uppermost horizon, the A_{11}, is greater than the two horizons beneath. Furthermore, the A_{12} is somewhat higher in phosphorus than the AC. This gradual decrease in phosphorus content with depth strongly suggests enrichment from above through the physiologic processes of plants.

The phosphorus content of the soil, especially the surface horizon (A_{11}), decreases upslope toward the Wells residual soil. Continuing upslope (profiles 22 through 27, fig 5) to the soil farthest from the Phosphoria formation, the phosphorus content decreases gradually until a minimum is reached, 1,000 ppm for the surface and 250 ppm for the deeper horizons. The decrease in phosphorus content of the soil away from the phosphatic shales may indicate that there is insufficient phosphorus in the Wells formation to permit significant enrichment by plants of the upper soil horizons.

Zinc content of the Wells colluvial soil overlying the phosphatic shale member is of the order of 400 to 800 ppm in the three upper horizons of all profiles (fig 5). Unlike phosphorus, zinc content for the surface horizon (A_{11}) is nearly constant across the entire section; however, the zinc gradually decreases away from the phosphatic shale member to a low of about 100 ppm. A slight peak for zinc also occurs in the No. 8 profile that gave the phosphorus peak. The A_{12} horizon is somewhat lower in total zinc with slight peaks at the same points as the A_{11}, otherwise the zinc content is nearly identical with the surface horizon. The AC horizon has a total zinc content lower than for the A_{11} and A_{12} horizons, and there are several peaks on this curve.

Generally, zinc behaves similarly to phosphorus, with plant enrichment of the Wells colluvium from the zinc-rich phosphatic beds beneath. This enrichment is, therefore, from the surface downward. Movement within different profiles does not proceed at the same rate; this results in some deeper horizons being lower in zinc content than the same horizon for other profiles. The phosphatic shale colluvium beneath the Wells colluvium has a nearly constant

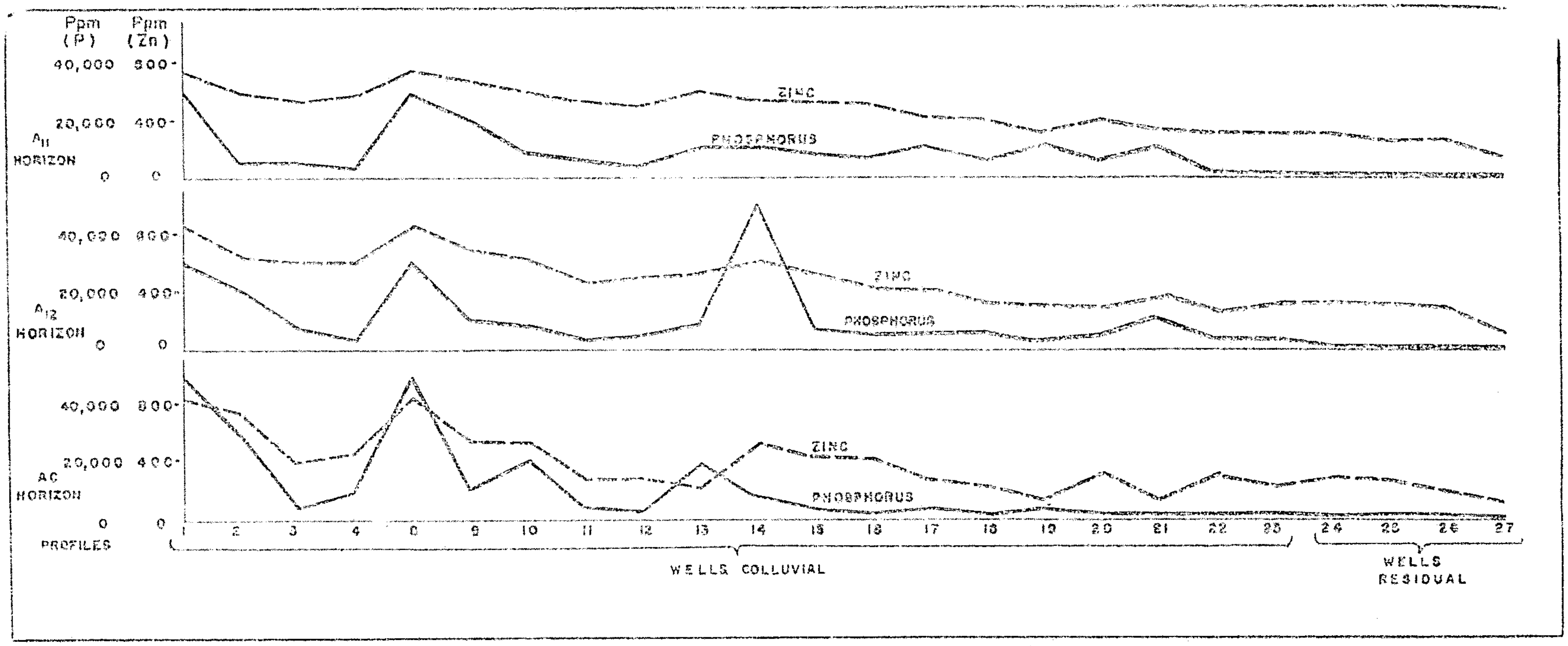


FIGURE 5. PHOSPHORUS AND ZINC CONTENT OF THE SOIL AT THE EAST GEORGETOWN TRENCH

zinc content, and therefore, the peaks of the zinc curves are not related to the zinc content of the phosphate rocks immediately beneath these peaks.

The copper and nickel content of these soils (fig. 6) is low, as hight be expected when one considers that the maximum copper and nickel content of the phosphatic shales does not exceed 500 and 350 ppm, respectively. The copper concentration of the A_{11} horizons less than 25 ppm profiles 1 to 12. There is an increase in the copper content of this horizon near the middle of the section, with a maximum of 100 ppm. The A_{12} and AC horizons show a similar trend. There are a few profiles where copper content reaches 150 ppm. These copper peaks are not related to the underlying phosphat beds because they do not occur in profiles over high-copper material. Moreover, several profiles containing low copper are over colluvial phosphate rock containing 150 to 200 ppm copper. The Wells residual soil contains nearly as much copper as the Wells colluvial soil; it may, therefore, be concluded that the soil is not being materially enriched with copper.

Less nickel is present in the Phosphoria formation than copper, but it behaves like copper (fig 6). There is less than 20 ppm nickel in most Wells colluvial soil.

Evidently the concentrations of copper and nickel in the Phosphoria formation are less than the minimum amount necessary to cause a significant enrichment of the overlying soil. Furthermore, the effects of the high phophorus content of these soils on the chemical properties of copper and nickel in these soils has not been evaluated.

Chromium and vanadium closely parallel one another in the series of profiles both in behavior and concentrations in the three horizons as shown on figure 7. The total quantity of chromium is slightly higher than vanadium for the Wells colluvial soil but is exceeded by vanadium in the Wells residual soil. The chromium content in the A_{12} horizon of profile 14 is 1,000 ppm and in the AC horizon of profile 9,750 ppm; most horizons, however, contain less than 200 ppm chromium. Although most profiles contain about 100 to 150 ppm vanadium, profile No. 1 in the AC horizon contains a maximum of 300 ppm for the section. Chromium and vanadium concentrations in the Wells residual soil are 35 and 50 ppm, respectively.

Although the concentrations of these two metals in the phosphate rocks is nearly the same, the Wells colluvial soil over the phosphates is enriched with chromium to a greater degree than with vanadium. Because the vanadium and charomium content is, with exceptions noted above, nearly constant across the entire section, maximum concentration of these elements do not appear to be related to the material immediately beneath the soils.

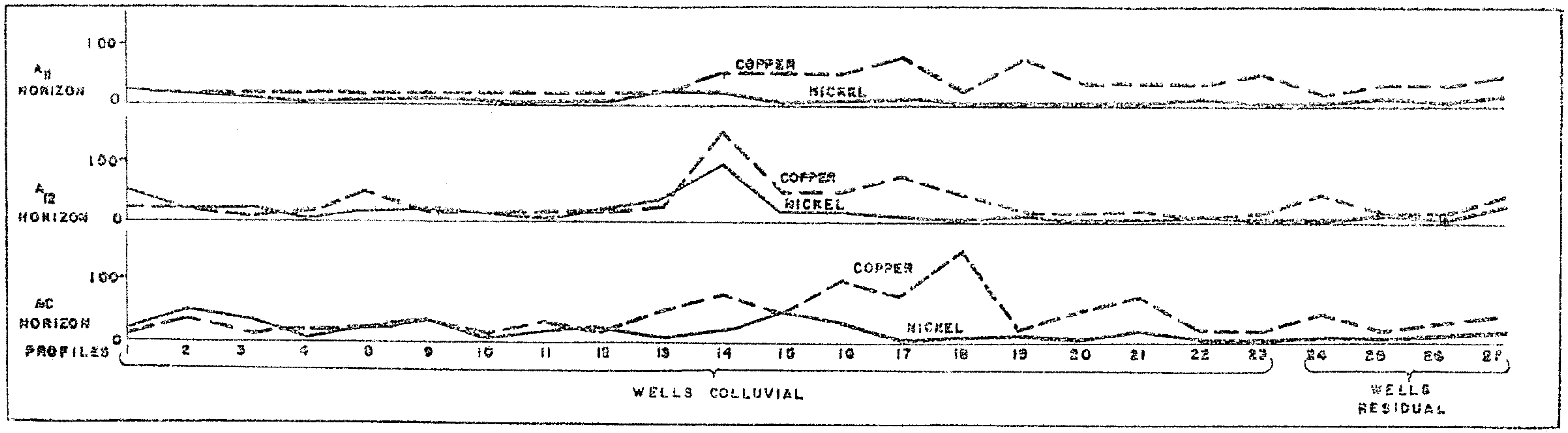


FIGURE 6. COPPER AND NICKEL CONTENT OF THE SOIL AT THE EAST GEORGETOWN TRENCH

CONCLUSIONS

There is a definite gradient from the surface downward for zinc and phosphorus. This strongly suggests that the plants are taking up these elements through their roots from the phosphatic shales and following the descomposition of the plant leaves and twings, enriching the surface of the Wells colluvial soil. Although this mechanism may also be operative for copper and nickel, there is no significant enrichment of the Wells colluvium with these elements. Either the copper and nickel content of the phosphatic shales is too low to permit enrichment, or the high phosphate content of the profiles may hinder the movement of copper and nickel.

There is a definite enrichment of the Wells colluvial soil with vanadium and chromium, but the data do not permit clear-cut conclusions to be drawn regarding the mechanism of enrichment. There is no gradient either upward or dawnward for vanadium and chromium. Either capillarity is as effective as plant processes for vanadium and chromium. Either capillarity is as effective as plant processes for vanadium and chromium enrichment, or these elements move readily through the profile once they are deposited on the surface. If the latter is true, capillarity would be ineffective as a mechanism of enrichment because it would have to operate in opposition to dawnward percolating ground water.

There must be a minimum quantity of a give metal present in the substratum before enrichment from the underlying material is significant in geochemical exploration. In this study, 200 to 250 ppm copper and 100 to 150 ppm nickel in the substratum were insufficient to cause significant enrichment of the overlying colluvial soil although several profiles were less than two feet thick. Zinc, on the other hand, did show a significant increase in metal content in the surface horizon even though its maximum concentration is only 3,500 ppm in the substratum. The vanadium and chromium content of the substratum, an average of 750 ppm for vanadium and 1,000 ppm for Cr, was also high enough to cause enrichment of the overlying soil.

SUMMARY

These data have answered, at least in part, the questions posed in the introduction, namely: How does a dry versus a moist climate affect the metal content of a soil? What mechanims operate to enrich a barren colluvial soil over a metal-rich substratum? and what is the minimum quantity of a metal in the substratum that will enable this metal to be present in the overlying soil in sufficient amounts to be significant in geochemical exploration?

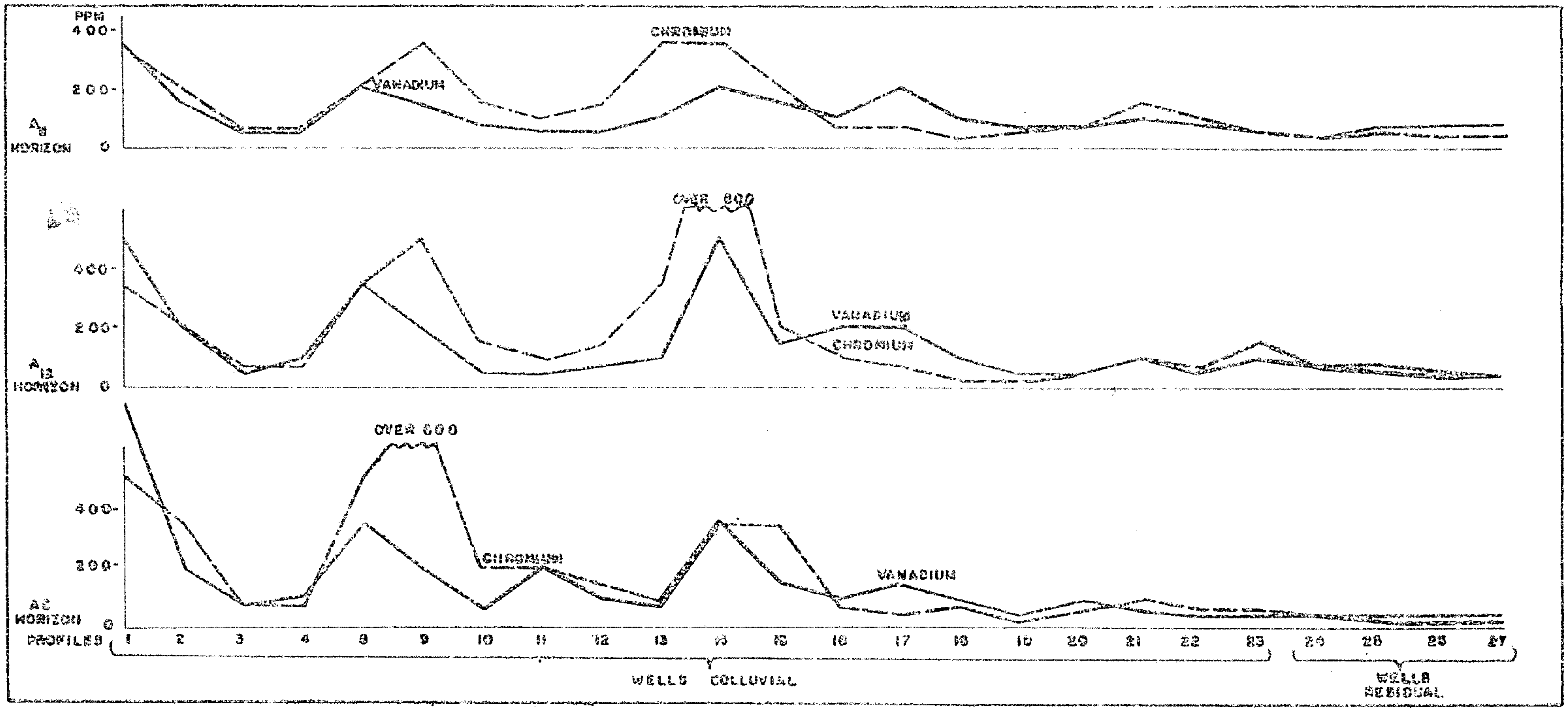


FIGURE 7. CHROMIUM AND VANADIUM CONTENT OF THE SOIL AT THE EAST GEORGETOWN TRENCH

There is a higher degree of enrichment of phosphorus, vanadium, chromium, and zinc in the surface soils under a dry than a moist climate. The higher content of these metals in a semiarid climate may be because capillarity is more effective in a dry climate. The limited rainfall of a semiarid region prevents deep penetration of moisture, and subsequent evaporation of capillary water in the soil horizons leaves the metals. Enrichment by plant processes in a semiarid region would not be effective because of the sparse plant cover which is active only during rainy periods.

In a subhumid climate, however, both plant processes and capillarity would be effective agents of metallic enrichment of a barren residual soil. The plant processes would be more effective than capillarity because the downward percolating would tend to nullify the upward movement of capillary water. The plant cover is also dense and would be effective accumulators of the substratum metals.

In both the arid and subhumid areas the Phosphoria formation contains at least a sufficient quantity of phosphorus, vanadium, chromium, and zinc to enable these metals to occur in abnormal quantities in the overlying soils. The substratum may not, however, contain sufficient quantities of copper and nickel to enrich the overying soils, or phosphorus may inhibit the movement of these metals; therefore, they are not significantly higher in the overlying soils.

OBSERVATIONS ON GEOCHEMICAL EXPLORATION IN TROPICAL TERRAINS

J. S. Webb *

ABSTRACT

A number of preliminary examinations and some detailed studies, principally in East, West and South-Central Africa, have demonstrated a wide field of application for geochemical exploration techniques in tropical terrain.

Examples are given, mainly from unpublished material, covering a variety of mineralizations and conditions, including copper-cobalt, lead-zinc, gold-arsenic-antimony, molybdenum, tungsten, tin, niobium, chromium and diamond-bearing kimberlite. Certain features of the observed metal dispersion are briefly discussed, with special reference to the influence of soil type, climate, topography, vegetation and bedrock geology.

From the practical point of view, the results illustrate (a) the applicability of systematic soil sampling in many areas, (b) the use that may sometimes be made of geochemical data in geologic mapping, and (c) the potential value of systematic drainage sampling in regional reconnaissance surveys.

In recent years, the application of geochemical prospecting in difficult tropical terrain has attracted a growing interest, and in some areas geochemical methods are now established as an integral part of prospecting procedure. Although a considerable amount of research and actual exploration has now been done in such terrain, little has been published apart from the early work of Roberts (1953), Webb and Millman (1950, 1951), and Hawkes (1954), in an area of lead-zinc mineralization in Nigeria. Subsequent activities by the Mining Geology Department and, latterly, the Geochemical Prospecting Research Centre, at Imperial College have covered a broader field and, although many of the investigations are still in progress, a brief review of some of the results so far obtained may have a general interest at this stage.

The contents of this paper are drawn largely from the work of the following post-graduate students and staff at Imperial College, to whom all credit is due for their individual contributions to the programme of research directed by the writer under the aegis of Professor D. Williams, Head of Department: J. S. Tooms (1955) (Northern Rhodesia and Sierra Leone), R. H. C. Holman (1956) (Uganda and Sierra Leone), J. D. Jacobson (1956) (Uganda), C. H. James (Southern Rhodesia), G. J. Govett (Northern Rhodesia) and A. L. Mather (Sierra Leone); supported by R. E. Stanton, Mrs. M. A. Gilbert and

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other members of the analytical staff in London. In addition to this research, the writer has also been concerned with geochemical examinations in other tropical territories, mostly in Africa.

ACKNOWLEDGEMENTS

The Geochemical Prospecting Research Centre at Imperial College is assisted by generous grants from the Colonial Office and the Department of Scientific and Industrial Research. The writer would also like to record the debt of gratitude owed to the many Companies, Geological Surveys and the other Government organizations and their staffs for the collaboration and generous assistance that have made the fieldwork possible. Particular acknowledgement is made to Messrs. Mines Development Syndicate, Ltd., Rhodesian Selection Trust, Ltd., Consolidated African Selection Trust, Ltd., Kilembe Mines, Ltd., and New Consolidated Gold Fields, Ltd.; and to the Colonial Geological Surveys of Nigeria, Uganda, Tanganyika, Sierra Leone, Bechuanaland and Borneo.

Finally, it is a real pleasure to express sincere appreciation of the stimulating help and support received from Dr. Dixey and his staff on the Directorate of Colonial Geological Surveys.

SELECTED EXAMPLES ILLUSTRATING METAL DISPERSION UNDER TROPICAL CONDITIONS

About one half of our work has been concerned with metal dispersion in areas of copper mineralization, and data for other metals, including lead, zinc, arsenic, antimony, cobalt, nickel, chromium, tungsten, molybdenum, tin and niobium are generally less comprehensive and, in some instances, fragmentary. In general terms, therefore, the results must be considered as more or less provisional.

Of necessity, the following review is based on much abbreviated and extremely selective extracts from a large volume of information. As a result, it is inevitable that only some of the more important general features have been touched upon, and many important local variations have had to be omitted altogether.

Primary metal dispersion patterns, being the result of deep-seated geological phenomena, do not fall within the scope of this paper, which is mainly concerned with dispersion in the zone of weathering and the influence of climatic conditions. The results of primary dispersion studies are, however, included where the distribution of trace metals in the bedrock has contributed to the local pattern of secondary metal dispersion.

SECONDARY DISPERSION IN SOIL

A characteristic combination of deep weathering and thick soil covering constitutes one of the major difficulties commonly encountered in mineral exploration under tropical conditions. In consequence, the possibility of applying systematic geochemical soil surveys attracted first attention in our research programme.

(1) COPPER AND COBALT

By virtue of extreme contrasts in physical environment, results obtained in the Rhodesian Copperbelt[1] and in the Ruwenzori area of Uganda serve to illustrate several features of metal dispersion in soil (and, later, in sediments) related to flat peneplain conditions on the one hand and rugged mountainous terrain on the other.

With some exceptions, the *Northern Rhodesian* copper-cobalt deposits occur as sulphide disseminations in stratigraphic horizons near the base of a folded sedimentary succession. The sediments form synclinal inliers in the granite and schists of the Basement Complex; gabbros occur as local intrusives. Bornite, chalcocite, chalcopyrite and pyrite with minor amounts of cobalt-bearing minerals, are disseminated in both argillaceous and arenaceous host-rocks, the average tenor in the study area being about 2.5% Cu and 0.2% Co.

The ore is intensely leached and oxidized to 300 ft. or more from the surface and, together with the highly weathered bedrock, is nearly everywhere overlain by a deep persistent overburden.

The topography and dendritic drainage is that of a typical peneplain. Freely drained areas of deep residual lateritic soil slope gently toward shallow drainage depressions occupied by seasonal swamps. Here, organic-rich glei soils, characteristic of impeded drainage conditions, are developed in an overburden which is a variable mixture of residual material and transported (colluvial) soil derived from the adjoining ground. The climate is markedly seasonal, with an average annual rainfall of 50 in., and the vegetation is relatively thin, forest savannah, except in the seasonal swamps which support only grasses. These seasonal swamps occupy but a small proportion of the total area. The technical problem of locating individual mineral deposits is, therefore, largely concerned with prospecting in ground covered by the residual lateritic soil.

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[1] Geochemical prospecting on the Rhodesian Copperbelt was initiated by Messrs. Rhodesian Selection Trust Services, Ltd. The results given in this paper refer to our own investigations carried out with the Company's support but using distinctly different methods to those originally employed by them. (8)

TABLE I (a)

DISTRIBUTION OF COPPER IN WELL-DRAINED LATERITIC SOIL PROFILES, NORTHERN RHODESIA

Horizon	Description	Average depth	Average background profile		Anomalous profiles near mineralization			
					Argillaceous bedrock		Arenaceus bedrock	
			Total Cu* (ppm)	Readily soluble Cu* (ppm)	Total Cu (ppm)	Readily soluble Cu (ppm)	Total Cu (ppm)	Readily soluble Cu (ppm)
Ao	Grey-buff, sandy	0– 3 ins.	50	4	460	30	150	2
		3– 9 ins.	35	1.5	500	20		
Ai	Yellow-brown, sandy (Stone-line)	1–10 ft.	45	<1	650	15	200	<1
B	Red, nodular, lateritic loam	10–15 ft.	50	<1	800	50	640	2.5
C	Mottled red/yellow clay or sandy clay	15–20 ft. approx.	60	<1	1200	80	1700	5

* All copper contents refer to minus 80-mesh fraction.

NOTE: Ferruginous nodules in the B horizon contain *erratic* values of 50-500 ppm. Cu in background profiles, and up to 2000 ppm in anomalous profiles. Very pronounced enrichment of Cu is also noted in manganiferous segregations (up to 3500 ppm Cu).

TABLE I (b)

DISTRIBUTION OF COPPER IN SEASONAL SWAMP SOIL PROFILES, NORTHERN RHODESIA

Soil Horizon	Description	Average depth (ft.)	Background profile		Draining mineralized ground		Overlying Sub-outcropping mineralization	
			Total Cu* (ppm)	Readily soluble Cu* (ppm)	Total Cu (ppm)	Readily soluble Cu (ppm)	Total Cu (ppm)	Readily soluble Cu (ppm)
Ao	Black organic-rich topsoil (organic carbon about 3%)	0 – 2	90	4	1150	360	3500	1200
G	Blue-gray, orange spotted, sandy/clay subsoil	2 – 6+	80	4	800	170	2500	900

* All copper contents refer to minus 80-mesh fraction.

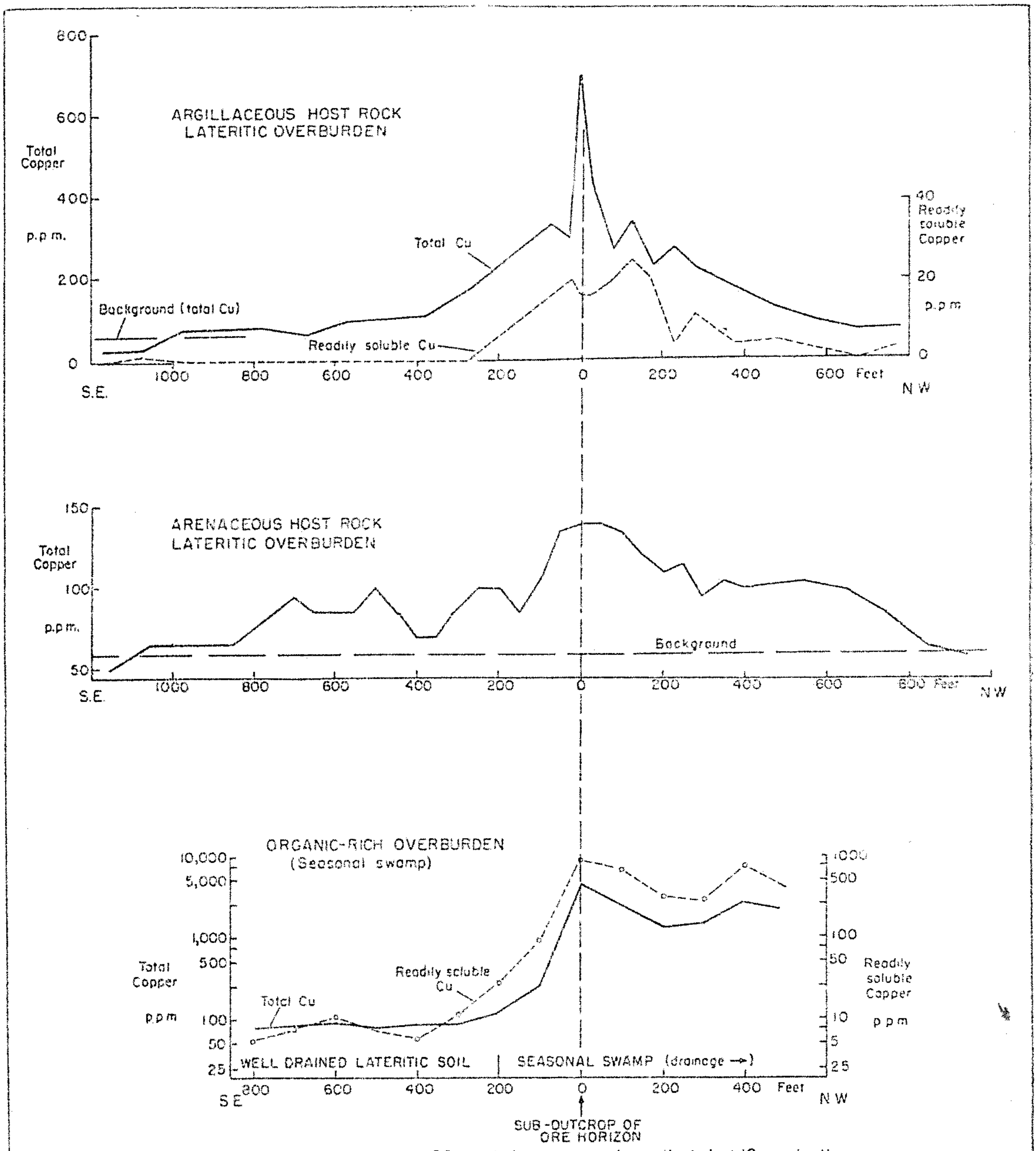
The overburden may attain thicknesses of up to 20 ft and more, and there is a marked development of well differentiated horizons in the soil profiles (Table I). Study of metal distribution within these profiles shows that, with the exception of enrichment in ferruginous nodules and sporadic manganiferous material in the lower horizons, copper tends to increase in the finer size fractions throughout the profile. However, the metal content in the minus 80-mesh fraction gives adequate contrast for prospecting purposes.

Copper also increases progressively with depth in lateritic overburden. The effect of leaching in the upper horizons is more pronounced in anomalous than in barren profiles, and is particularly marked over mineralization in arenaceous bedrock. However, the metal content in the A horizon is always anomalous over mineralization, irrespective of the nature of the host-rock. Consequently, a depth of 12-18 in. is normally used in prospecting. The same depth is ideally suited to seasonal swamp soils where there is a very strong contrast between barren and anomalous profiles in all horizons.

Typical anomalies obtained by near-surface sampling in the A horizon are shown in Fig. 1. Over argillaceous host-rock, relatively sharp peak values mark the sub-outcrop of mineralization, and the broad base of the anomaly extends for at least several hundreds of feet on either side of the sub-outcrop in flat terrain. Lower values and more irregular metal distribution patterns appear to be characteristic in arenaceous areas, although the anomalies are nonetheless extensive. The reliable detection of relatively weak "statistical" anomalies of this type require more careful analysis, and the collection of an appropriately larger number of samples within the anomalous zone.

In both argillaceous and arenaceous areas, particularly the latter, more intense and better defined anomalies are obtained by sampling in the B and C horizons. The depth at which these horizons occur, however, is usually too great and too variable for the purposes of routine prospecting, although deep sampling across a near-surface anomaly may help to pin-point the sub-outcrop of mineralization more closely.

Over much of the area the ground is rarely inclined at more than 1-2 degrees, yet even on these gentle slopes there is often a very considerable downslope extension of the anomalies (Fig. 2). Although some lateral dispersion of metal undoubtedly takes place in the upper soil horizons near the sub-outcrop of the ore, the even tenor of the anomaly for 2,000 ft or more downslope indicates some further dispersion process. It seems probable that deep-rooted plants may assist in this respect by taking up copper from the metal-bearing ground-waters draining the mineralized area and subsequently returning the metal to the soil, where a proportion may be fixed in near-surface horizons.



N B — All analyses carried out on minus 80-mesh fraction, samples collected at 12 ins depth

FIGURE 1—METAL CONTENT OF SOIL OVER COPPER DEPOSITS IN NORTHERN RHODESIA

Fixation of copper by organic matter is undoubtedly responsible for the very intense anomalies developed in swamp soils (Fig. 1). The seasonal rise-and-fall of groundwater readily accounts for the translocation of copper from bedrock up into the transported or partially transported overburden.

Table I and Fig. 1 include some preliminary data for readily-soluble copper as distinct from "total" metal. Contrast between barren and anomalous soils and the ratio of readily-soluble to total metal content is very variable and dependent on soil horizon, soil type and the nature of the host-rock. Nevertheless, the data indicate that, whereas it would be dangerous in prospecting to rely on the distribution of readily soluble metal in lateritic soils, simple cold-extraction methods may be usefully employed for on-the-spot field tests, particularly for reconnaissance work in seasonal swamp soils.

By comparison with the volume of data on copper, rather less information is available concerning cobalt. In general terms, however, cobalt tends to follow copper, maintaining in the soil approximately similar ratios to those in the primary ore. Over mineralization the Co:Ni ratio is generally $>$ 1, and this criterion assists in distinguishing between small significant anomalies (150 ppm Cu.) related to mineralization and apparent anomalies reflecting gabbro bedrock (Co:Ni ratio $<$ 1).

Termitaries are a common feature in Northern Rhodesia, and the possibility of using termitary samples in prospecting has been considered on a number of occasions. Although the termites undoubtedly move a considerable amount of material below 12 in. from surface, probably even to ground-water level, the greater part of their activity is restricted to the A horizon. It is considered that the observed patchy distribution of high values within the termitary and the need to survey the position of each sampling point more than offset any advantage due to some material being brought up from deeper levels in the soil where anomalous copper contents are usually higher than at surface.

In *Uganda,* the mineralization at Kilembe in the Ruwenzori Mountains has some features in common with the Rhodesian occurrences, although the physical conditions are entirely different. At Kilembe, the deposits take the form of sulphide disseminations or massive bands which, broadly speaking, follow the structure in a folded metamorphic complex. The average tenor of the known ore is about 2% copper and 0.2% cobalt. At the surface the ore body is gossanized, but oxidation extends only to relatively shallow depths of about 60 ft.

Despite mountainous topography, the ground is often poorly exposed, even on 20-40 degree slopes. The depth of overburden is variable, but averages about 4 ft thick. The soil is residual in origin, consisting of a red loam with poorly-differentiated horizons (Table II). Soil creep is active and, locally, there is

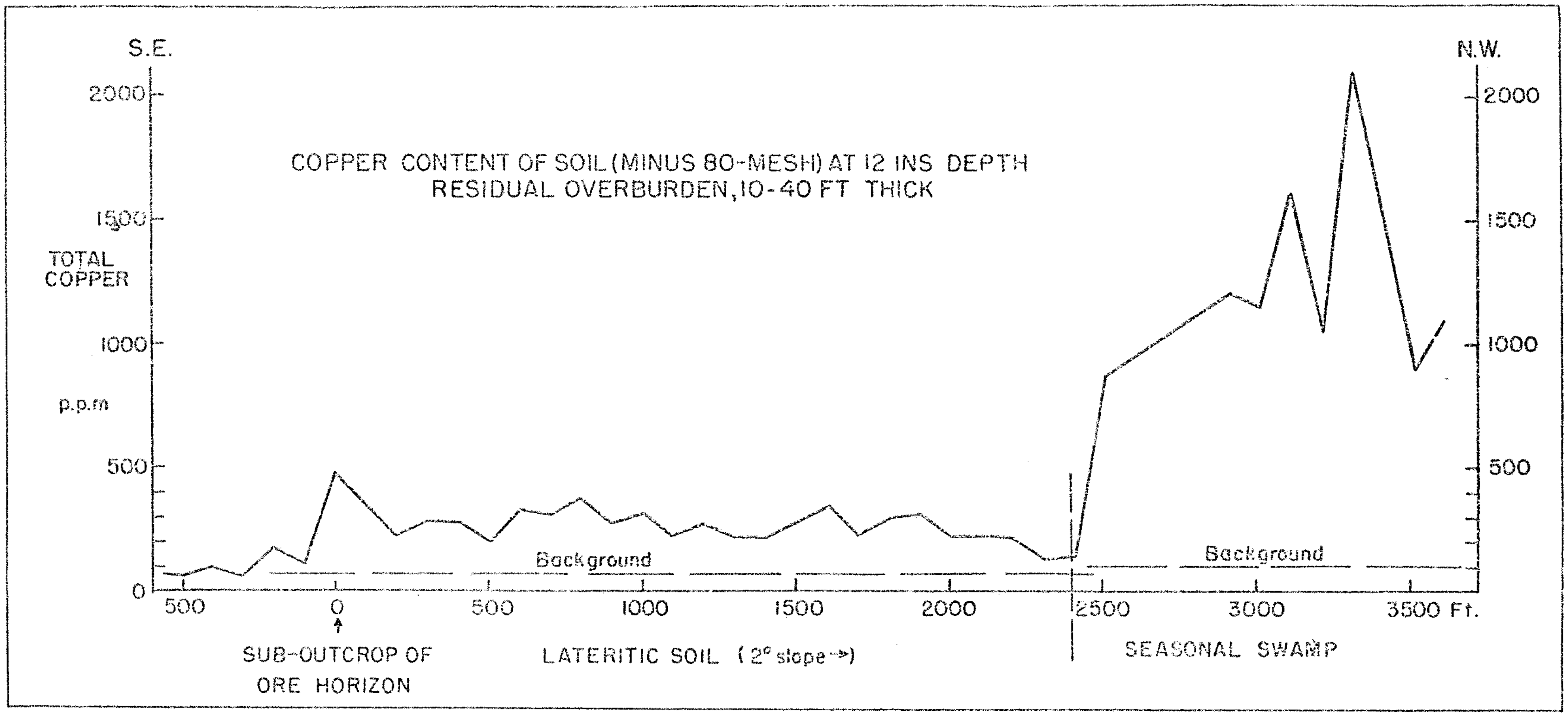


FIGURE 2.-ACCUMULATION OF COPPER IN SWAMP SOILS DOWN-DRAINAGE FROM MINERALIZATION IN NORTHERN RHODESIA.

evidence of land slip, but in general a shallow-rooted grass vegetation keeps the surface relatively stable. The study area is situated at an altitude of 7,000 ft, where the original forest cover has mostly been destroyed by former native agriculture. The climate is seasonal, but not so well-defined as in Northern Rhodesia, and although the total annual precipitation is similar, 50 inches, it is spread rather more evenly over the year.

As in Northern Rhodesia, metal dispersion patterns in soil were examined in the vicinity of known, but virgin, mineralization. Analysis of the different size fractions again showed the copper content to increase with decreasing particle size. The distribution of copper in the minus 80-mesh fraction throughout the soil profile over the barren and mineralized rocks is given in Table II. Characteristic relationships were noted between the metal content and bedrock type in barren areas, the copper content increasing from acid to basic parent material. Over mineralized bedrock the metal content tends to increase progressively with depth, and the effect of leaching is particularly marked in the top 6-12 inches. Downslope from mineralization, however, peak values are recorded in the B horizon 20-30 inches from the surface, reflecting downslope migration of metal in the zone of lateral sub-surface drainage and soil creep.

Unlike the lateritic profile in Northern Rhodesia, the B horizon in the Uganda area lies within 2 ft of the surface, and is readily available for systematic sampling. The pattern of lateral metal distribution obtained by analysis of B horizon samples taken at 18 inches depth is illustrated in Fig. 3. At the 200 ppm level, the anomalies are several hundreds of feet wide, and show sharp peaks rising to 400-1,500 ppm over mineralized bedrock. Although there is undoubted downslope migration of metal in the soil, the anomalies are not always so markedly asymmetrical as might be expected on such steep slopes. This must be due in part to primary dispersion aureoles in the bedrock, since the appreciable upslope extension of some anomalies can only be explained in this way. High rates of mechanical dilution and chemical leaching can be expected to accompany soil creep under tropical conditions of weathering, and this factor probably contributes to the relatively symmetrical form of the anomalies by militating against the fixation of high values in the soil downslope from mineralization.

Fig. 3 also shows the characteristically high nickel-cobalt ratio accompanying a small copper anomaly related to dolerite, while over significant sulphide mineralization the ratio is usually reversed. As in Rhodesia, cobalt tends to follow copper during dispersion and again the ratio of these metals in the ore is usually similar to that in the soil.

In B horizon soils, the proportion of readily-soluble copper, although variable, is more consistenly reliable than in the lateritic soils of Nothern Rhodesia. The

Table II

DISTRIBUTION OF COPPER IN THE SOIL PROFILE, RUWENZORI MOUNTAINS, UGANDA

Horizon	Description	Average depth in.	Background profiles			Profiles near mineralization		
			Gneiss bedrock	Granulite bedrock	Dolerite bedrock			
			Cu ppm	Cu ppm	Cu ppm	Cu ppm	Cu ppm	Cu ppm
A_1	Dark gray, sandy loam	0– 3	10	25	110	150	120	700
A_3	Red-brown clay loam (Stone-line, if present)	3–15	25	60	145	180	290	1000
B	Red, sticky (sandy) clay	15–50	10	60	185	280	550	1125
C	Weathered bed-rock fragments in excess of clay matrix	50+	10	60	225	500	700	

All copper contents refer to minus 80-mesh fraction correspondence between copper dispersion patterns for both forms of the metal is indicated in Fig. 3, from which it would seem that simple cold-extraction analysis could be usefully employed for the rapid preliminary "scanning" of routine soil samples.

Whereas geochemical soil surveys for copper are relatively straightforward in their application and interpretation in the Rhodesian and Uganda field areas, preliminary work[2] in an area of copper mineralization in *Bechuanaland* has indicated a number of problems not previously encountered to the same degree elsewhere. The area lies on the fringe of the Kalahari basin, where the low seasonal rainfall (av. 17 inches) has caused the development of well-differentiated calcified soil profiles, very different from the ferruginous lateritic profiles developed from similar parent material in Rhodesia and elsewhere.

The essentially flat topography is that of an ancient peneplain, and the bedrock geology is largely concealed beneath a persistent overburden. The cover, which is often several feet thick, is clearly residual in the freely drained areas, where pale brown, sandy, calcareous soils are the rule. The origin of the black calcareous clay profiles, typically found in the broad areas of slightly lower ground, is more obscure, but it is probable that the clay is a variable mixture of colluvial and residual material.

Mineralization occurs as veins and disseminations of copper sulphides in a steeply-dipping shear zone coinciding with a raft of metamorphosed sediments in granitic gneiss. The ore is intensely oxidized to a considerable depth.

Over non-mineralized rock, background values lie in the range 20-50 ppm, and there is very little change down the profile. The distribution of metal in near-surface residual soils around a zone of probably feeble mineralization is shown in Fig. 4. The ground slopes very gently to the west but, unlike the Rhodesian anomalies, there is much less downslope extension of the anomalies, due no doubt to the deeper groundwater level and the much higher soil pH (8.0-9.2, cf. 4.5-6.5 in Rhodesia) which must considerably restrict sub-surface dispersion of copper in aqueous solution. Further evidence for this assumption is given in Table III, which shows the distribution of metal in the profile in an area of suspected surface contamination. The fact that copper is mobile to a degree, however, is shown by the high values obtained in occasional, saucer-shaped drainage 'pans' some distance from mineralization.

No definitely positive results have been obtained from exploratory sampling in the black clay soil areas, but it is not yet known whether this is due to inhibited metal dispersion in this soil type or to failure of the known mineralization to continue along the strike towards the sample traverses.

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[2] In collaboration with C. C. Boocock, Geological Survey, Bechuanaland Protectorate.

TABLE III

METAL DISTRIBUTION IN THE SOIL PROFILE IN AREAS OF SUSPECTED SURFACE CONTAMINATION:

(a) ancient copper smelting (?) Bechuanaland; (b) arsenical smelter smoke, Southern Rhodesia.

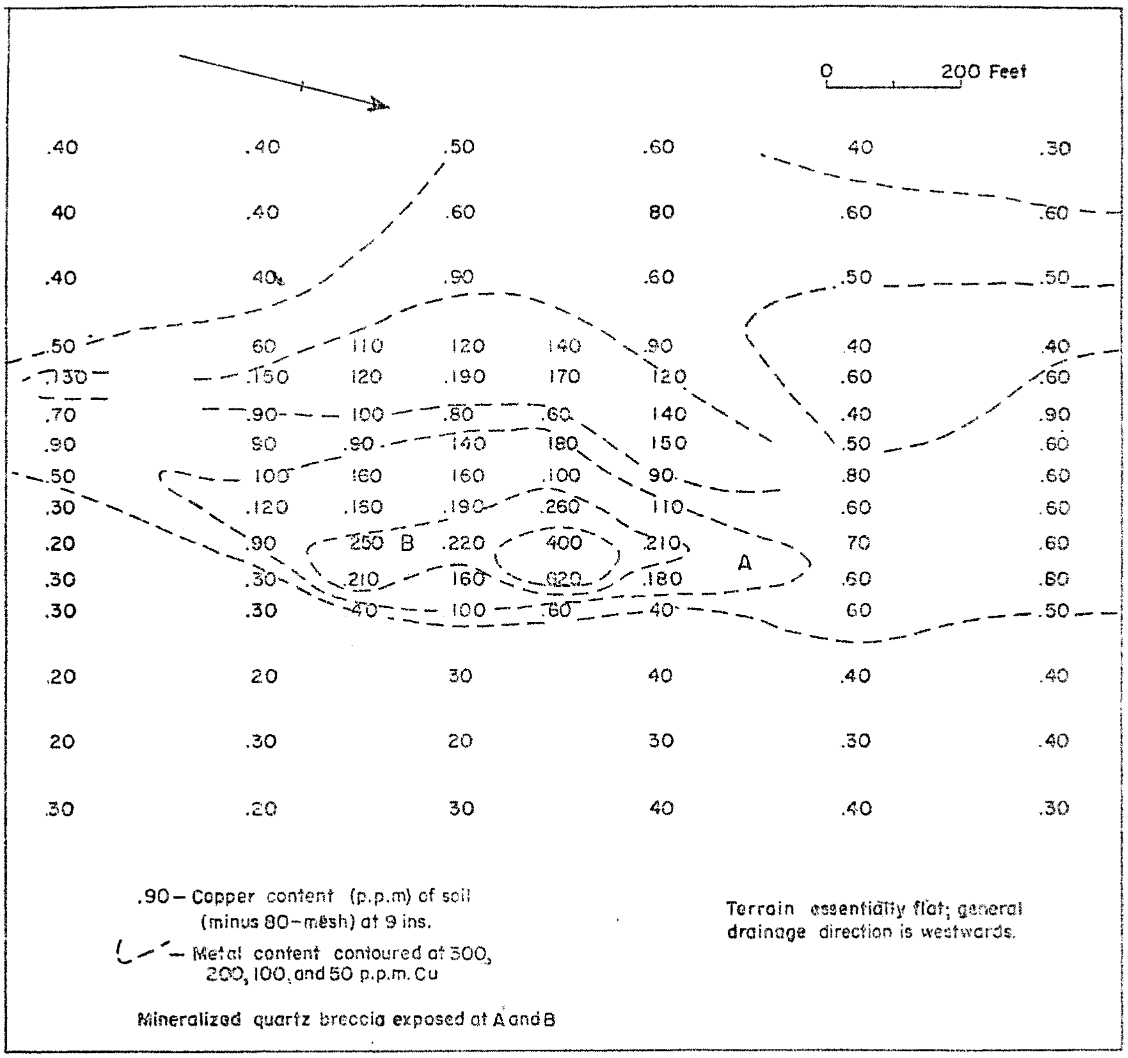
(a)				(b)		
Description	pH	Depth in.	Cu ppm	Description	Depth in.	As ppm
Brown-black topsoil	8.0	0–6 6–12	7,500 1,600	Sandy layer transported by sheet wash	0–2	560
Brown-black clay subsoil	8.4	12–31	200	Brown loam subsoil	2–8 2–13	200 120
Brown sandy clay, some $CaCO_3$ spots	9.0	30–52	50	Red loam with rubble	13–18	50
Main zone of calcification with bedrock fragments.	9.0	52–63	40	Soft, mottled decomposed greenstone	18–28	45
Decomposed granite gneiss with patches of $CaCO_3$	9.2	63–82	40			

All metal contents refer to minus 80-mesh fraction.

(2) LEAD AND ZINC

The only detailed information available on base metal dispersions in tropical soils is that obtained by Hawkes (1954) in *Nigeria.* In slightly undulating terrain, surface anomalies up to 500 ft and more wide, with values ranging up to 500-1,000 ppm Pb and 100-200 ppm Zn were observed in a residual lateritic overburden concealing lead-zinc-siderite veins in shale host-rock; background values are 30 ppm for lead and 50 ppm for zinc.

In freely drained ground, the overburden consists of strongly degraded lateritic rubble, rarely more than 18 inches deep, that has been disturbed by native cultivation. However, similar geochemical results (Millman, 1953) have been obtained from samples collected by the writer in an area some 300 miles



.90 — Copper content (p.p.m) of soil (minus 80-mesh) at 9 ins.

Metal content contoured at 300, 200, 100, and 50 p.p.m. Cu

Mineralized quartz breccia exposed at A and B

Terrain essentially flat; general drainage direction is westwards.

FIGURE 4.—DISPERSION PATTERN FOR COPPER IN SOIL NEAR A COPPER MINERALIZATION IN BECHUANALAND PROTECTORATE.

TABLE IV

DISTRIBUTION OF LEAD IN A RESIDUAL, FREELY DRAINED SOIL PROFILE, S. AFRICA

Depth in.	Description	Lead content (ppm)				
		—20+35 mesh	—35+80 mesh	—80+135 mesh	—135+200 mesh	—200 mesh
0– 4	Blackish-brown topsoil	190	280	170	320	480
4–24	Red-brown sandy loam	140	70	90	130	190
24–36	Ferruginous nodular zone with Mn segregations	2250	2400	750	800	1100
36–48	Red loam (grading into soft, weathered norite)	290	120	180	140	180

NOTE: 1—Background contents for all horizons and all size fractions are 15 ppm Pb.

NOTE: 2—In the same profile, zinc contents range from 20 to 130 ppm. and, although showing some concetration in the finer size fractions in all horizonts, there is no evidence of any marked enrichment at 0-4 in. and 24-36 in. as shown by lead.

to the north-east, where the degraded lateritic soil cover may be several feet thick. In both areas, the rubble zone may occasionally be separated from the thick weathered bedrock by a few feet of consolidated lateritic clay.

In contrast to the lateritic soils, seasonal swamp profiles, similar to those noted under comparable conditions in Northern Rhodesia, develop in poorly drained areas. Change in soil type, however, has little effect on the anomalies for lead and zinc where the overburden is definitely residual. On the other hand, where the cover is essentially transported alluvium, the dispersions of zinc and, especially, lead is greatly restricted (Hawkes, 1954). Nevertheless, a narrow dispersion pattern was detected over a vein concealed beneath 6-8 ft of alluvium, the inferred age of which is 400 years.

Very different soil conditions prevail in areas recently sampled in *Tanganyika,*[3] where low grade lead-copper mineralization in shear zones is concealed by at least three types of cover. Preliminary examinations have demonstrated strong near-surface lead anomalies in the residual overburden that occurs on freely drained areas of moderate relief. Where studied, the soil profile is essentially a poorly-differentiated red loam with more or less rubble, grading downwards into highly decomposed granite gneiss. The depth of cover is variable, being shallow on the crests of low ridges and increasing to over 7 ft towards the base of the slopes. Decreasing metal values in the soil extend beyond the slopes for at least 300 ft into the broad areas of surrounding flat-lying ground, where a stiff lateritic clay horizon is encountered beneath several feet of red loam.

It has not yet been possible to find out whether metal dispersions are detectable over mineralization concealed under the very thick overburden of the flat-lying areas, where freely drained colluvial and typical seasonal swamp soils also occur.

An interesting feature in the distribution of lead is its variable tendency towards enrichment in one or more soil horizons. This feature is not at all uncommon in temperate climates, where surface enrichment up to one-hundred-fold and more may provide a major difficulty in interpreting the results of systematic geochemical soil surveys. The apparently inconsistent behaviour of lead in this respect is also borne out by experience under tropical conditions. In Tanganyika, for instance, the anomalous metal content increases more or less uniformly with depth, while in Sierra Leone there is evidence of surface enrichment (Table V). As an extreme example, a profile taken from the centre of a strong anomaly over a lead vein in *South Africa* shows marked preferential enrichment of lead in the topsoil, and even more strongly in a sub-surface nod-

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[3] In collaboration with A. P. Fawley, Geological Survey of Tanganyika.

ular horizon (Table IV). In this profile, there is also an accompanying tendency towards enrichment in the coarser as well as the finest size fractions.

Zinc, on the other hand, rarely shows any marked preferential enrichment and, where studied, the concentration generally increases with depth and in the finer size-fractions. Also in contrast to lead, both zinc and copper are at times extremely tightly held in tropical soils and may then require a fusion followed by an acid leach for reliable extraction in analysis. Cu

(3) ARSENIC AND ANTIMONY

In a number of areas in Africa, notably *Southern Rhodesia* and *West Africa*, gold occurs in association with arsenic and, occasionally, antimony. In the absence of a rapid field test for gold and because, in some areas, gold is subject to leaching and redistribution near the surface, arsenic and antimony have been examined as "pathfinder" elements for gold. It will be appreciated that although the existence of arsenic and antimony anomalies in the soil do not necessarily imply the presence of auriferous mineralization, they may assist

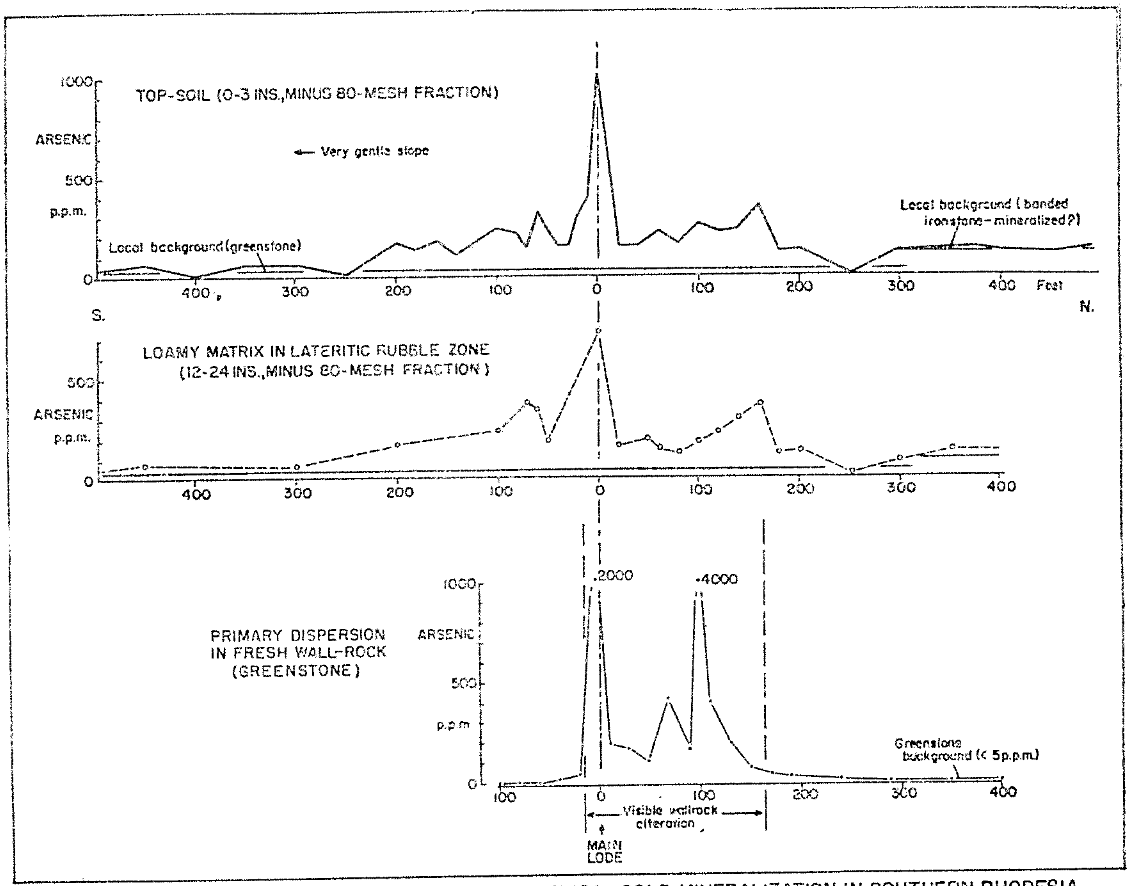

FIGURE 5.—ARSENIC ANOMALIES RELATED TO ARSENICAL GOLD MINERALIZATION IN SOUTHERN RHODESIA.

the tracing of mineralized structures and provide focal points for direct exploration by drilling or other means. Current investigations in Southern Rhodesia and Sierra Leone have yielded encouraging results in this respect.

In the Rhodesian study areas, gold occurs associated with arsenopyrite and occasionally stibnite, in mineralized shear zones and quartz veins traversing greenstone or sandstone host-rocks. The terrain is flat to undulating, with occasional hills and ridges, and the solid rocks are, as a rule, concealed by a residual lateritic overburden varying from 2-8 ft deep. In many areas the profile is degraded and rubbly, but may sometimes be well-differentiated into red loam and ferruginous nodular horizons grading into decomposed bedrock.

In highly ferruginous soils developed over basic bedrock, there does not seem to be any very marked variation in arsenic content with depth, apart from a slight tendency towards enrichment in the topsoil and possibly in zones of maximum iron accumulation. Good anomalies are developed over mineralization in the soil at about 12 inches depth. There appears to be little leaching of arsenic during weathering, and such lateral dispersion as does take place is probably largely mechanical. This is consistent with experience elsewhere (in Idaho, U.S.A.; H. E. Hawkes, pers. comm.) and is well brought out by comparing the distributions of arsenic in lateritic soil and in mineralized rock below the zone of weathering observed in one of the Rhodesian study areas (Fig. 5) The relative immobility of arsenic is further illustrated by its retention in the upper part of the soil in an area affected by arsenical smelter smoke (Table III).

In contrast to this relatively restricted dispersion in highly ferruginous soils, due no doubt to the formation of insoluble iron arsenates, there is evidence that arsenic may be appreciably more mobile in soils developed over sandstones and other rocks possessing a relatively low iron content.

Similar results are being obtained in Sierra Leone, where lenticular gold-quartz veins with associated arsenopyrite and base metal sulphides occur in sheared talc-carbonate schists. The overburden, on the higher ground, consists of several feet of indurated laterite (duricrust) overlying 2-3 ft of nodular red loam grading into weathered bedrock. The area is being actively dissected and the duricrust horizon is missing on the youthful valley slopes. There is considerable contrast between the metal content in background and anomalous profiles (Table V) and strong anomalies up to 500 feet wide and rising to 600 ppm. As are detectable in valley slope soils, whilst current work indicates that near-surface anomalies are also developed in the duricrust horizon.

The few samples thus far analyzed for antimony provisionally indicate that only under special circumstances will this element prove to be a better indicator than arsenic. The reasons for this lie in the more sporadic distribution of antimony in the primary ore, and in the more tedious analytical procedure required for its determination.

(4) TUNGSTEN AND MOLYBDENUM

Preliminary soil studies in Uganda and Sierra Leone have given encouraging results for tungsten and molybdenum respectively.

In the Kigezi district of *Uganda*, low-grade ferberite deposits occur as veins and disseminations in shear-zones in phyllites. The youthful topography is hilly and covered by tropical forest except for areas disturbed by native cultivation. Bedrock is concealed by a persistent overburden averaging 4-10 feet in thickness, the soil being residual and dominantly composed of red loam, in which moderately well-defined horizons are often developed.

The regional background content is < 5 ppm W but rises to 5 - 10 ppm in the vicinity of mineralization; the extent of this high local back ground is not known. The sub-outcrop of the broad mineralized zone is reflected in the soil by anomalous areas several hundreds of feet wide, in wich the values range from 12 - 100 ppm W (Fig. 6(b) in samples collected at 1 foot depth. The metal is erratically distributed in the bedrock and this is responsible for a similar uneven distribution of high values in the soil. No preferential enrichment has been noted in particular soil horizons.

TABLE V

DISTRIBUTION OF METAL IN AN AREA OF ARSENICAL GOLD MINERALIZATION, SIERRA LEONE

Depth ft.	Description	Background profile				Anomalous profile			
		Cu ppm	Pb ppm	Zn ppm	As ppm	Cu ppm	Pb ppm	Zn ppm	As ppm
0–1	Red loam with numerous bedrock frags., with some humus	<10	<5	50	<10	100	400	80	300
1–3	Red loam with bedrock fragments	10	<5	55	<10	20	55	165	300
3–5	Soft, decomposed talc schist	20	10	50	<10	50	100	170	250

NOTE: All metal contents refer to minus 80-mesh fraction.

Table VI

AVERAGE BACKGROUND METAL CONTENT OF AFRICAN SOILS DERIVED FROM NON-MINERALIZED BEDROCKS

	Metal content of soil (minus 80-mesh fraction) at 12-24 in. depth (Parts per million)									
Rock types	Cu	Pb	Zn	Co	Ni	Cr	W	Mo	As	Sb
Sedimentary rocks:										
Sandstone	10–50	10–20	120	<20	<20	30–300	—	—	<5	<1
Shale	60–100	<5–110	15–160	<20	<50	——	—	—	—	<1–4?
Limestone	——	5–40	20–50	—	—	——	—	—	—	—
Metamorphic rocks:										
Quartzite	20–60	—	—	<20	<20	——	—	—	—	—
Phyllite	——	—	—	<20	<60	100–400	<2–6	—	—	—
Acid schist	30–60	10–60	15–110	<20	<20	15–35	—	—	—	—
Granite gneiss	10–25	5–30	50	<20	<20	——	—	—	—	—
Basic schist	30–150	<5	40–80	<70	100–200	300–600	—	—	<5	—
Metadolerite (greenstone)	20–110	5–15	30–50	—	—	——	—	<10	5	<1
Igneous rocks:										
Granite	25–50	—	—	<20	<20	15–40	<20	2–3	—	—
Dolerite	100–150	—	—	20–50	60–80	——	—	—	—	—
Gabbro	120–150	<10	<75	100	200	——	—	—	—	—
Dunite	——	—	—	250	750	——	—	—	—	—
Kimberlite	75	<25	<50	40	150	250–450	—	—	—	—

Note: The metal contents given above were obtained using the standard semi-quantitative prospecting methods of analysis and only representative of samples collected during the course of our areas mentioned in this paper.

Dispersion patterns for molybdenums are currently being investigated in *Sierra Leone*, where molybdenite occurs disseminated in granite or in pegmatitic deposits injected into amphibolite. As previously described, the lateritic overburden is residual and an indurated (duricrust) horizon figures prominently in the profile developed on the higher ground. Irregular anomalies with values up to 1,000 ppm Mo have been noted in near-surfaces samples collected at 6 - 12 inches depth in both red loam and duricrust soils. The peak values rise erratically from a broad anomalous zone in which the molybdenum content of the soil ranges from 30 - 200 ppm (Fig. 6(a), whereas the regional background concentration is <10 ppm.

(5) TIN, NIOBIUM

Only a few preliminary soil samples have been analyzed from vein and pegmatite areas in SW Uganda, but the results indicate the existence of (a) anomalous values for Sn and Nb over mineralization in areas of residual overburden and (b) erratic high values in outwash fans and in accumulations of colluvial soil at the base of slopes, downhill from sub-outcropping deposits.

(6) KIMBERLITE AND GEOLOGICAL MAPPING GENERALLY

The summary of background data for tropical soils given in Table VI shows that, given sufficient chemical contrast in bedrock lithology, geological trends may be reflected in the soil by minor variations in the pattern of trace metal distribution. Soils derived from ultrabasic bedrock are readily distinguished as a rule by a high nickel content in both temperate and tropical areas. Mention has already been made of the moderate copper and nickel contents, with Ni:Co >1, that may characterize soils derived from gabbro and dolerite bedrock. A high chromium content is another useful criterion of soils derived from basic rocks which have mapped geochemically during the course of work in a number of areas in Africa.

In passing, it may be mentioned that chromium has also been found to give strong anomalies over the sub-outcrop of chromite seams in serpentine (Great Dyke area of Southern Rhodesia), the maximum contrast occurring in the 80 - 135 mesh fraction of the soil.

Examination of Sierra Leone soils derived from kimberlite, basic schist, acid schist and granite show that kimberlite and basic schist can be readily distinguished from acid bedrock by the above-mentioned criteria. Furthermore, the kimberlite soils examined had a characteristically high base exchange capacity and, in depth, contained 50 per cent montmorillonite[4]. This probably accounts for the fact that only these soils give anomalous values by the rapid cold-extraction test for "exchangeable" zinc (Table VII). As the formation of montmorillonite is influenced not only by a higher magnesia content in parent rock, but also by pH and drainage conditions, it is not yet possible to say to what extent the Sierra Leone results are generally applicable to kimberlite occurrences elsewhere.

TABLE VII

METAL CONTENT OF RESIDUAL OVERBURDEN (MINUS 200-MESH FRACTION) DERIVED FROM KIMBERLITE AND OTHER ROCKS, SIERRA LEONE

	Depth ft.	Kimberlite	Basic schist	Acid schist	Granite
Nickel ppm	2	150	160	30	20
	4	260	180	30	20
	8	500	200	30	
Cobalt ppm	2	20	10	<10	10
	4	60	80	<10	<10
	8	50	10	<10	
Chromium ppm	2	340	900	60	50
	4	400	1050	110	55
	8	1000	1650	35	
Exchangeable zinc ppm	2	7	1	2	1
	4	5	1	1	1
	8	12	1	<1	
Base exchange capacity m.e/100g clay	2	8.4	3.6	2.7	6.8
	4	12.0	2.0	1.5	5.7
	8	28.8	2.9	0.5	
pH	2	6.2	5.0	5.2	5.2
	4	6.2	5.7	5.5	5.6
	8	5.5	5.9	6.1	

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[4] Determined by X-ray analysis of clay-size fraction kindly undertaken by Mr. G. Brown of Rothamsted Experimental Station.

CHEMICAL DISPERSION IN PLANTS

Many instances are known where the metal content of plants growing in the vicinity of sub-outcropping mineralization is greater than in similar species in non- mineralized areas. The question has frequently arisen as to the relative usefulness in prospecting of systematic plant analysis as compared with soil analysis. In Nigeria, comparison of the anomalies obtained by plant and soil samples along the same traverse line (Hawkes, 1954) shows that, whereas there is little correspondence for zinc, the anomalies given by lead are similar for both types of sample material. Subsequently, a number of soil/plant traverses in areas of copper, lead and arsenic mineralization showed that, although there is sometimes a degree of similarity in the metal distribution patterns, the plant anomalies are less reliable and more erratic than those detected in the supporting soil. This is particularly true for copper and zinc, and it is interesting to note that elements, such as lead, which are usually considered as toxic to plants, show the closer relationship in their distribution between the plant and the soil.

The fact that a relationship sometimes exists, however, draws attention to the part played by plants in metal dispersion. On old land surfaces in particular, the total amount of metal that has passed through the biochemical cycle must be considerable, and in areas of thick cover and deep-rooted vegetation plants may well influence the development of dispersion patterns in the soil to an important degree. This is particularly so in areas where sub-outcropping mineralization is covered by non-residual overburden (*vide.* the vertical "pipe-like" lead anomaly developed in alluvium above a lead-zinc vein in Nigeria (Hawkes, 1954).

GEOCHEMICAL DISPERSION IN THE DRAINAGE SYSTEM

Relatively little information is available concerning the applicability in tropical terrain of geochemical methods suited to regional mineral reconnaissance. These methods usually involve the systematic analysis of water and/or stream sediment samples with a view to detecting significant metal distribution patterns in streams draining mineralized areas.

Considering water analysis first, one of the major problems is the extremely pronounced temporal variation in the metal content of surface waters related to the characteristic seasonal nature of tropical climates. In Nigeria, the anomalous zinc content of streams draining mineralized ground may be subject to diurnal variations up to six-fold, when sampled early in the wet season (Webb and Millman, 1950). Entirely negative results were obtained, however, when further sampling was carried out in the dry season (Hawkes, 1954). A recent detailed study of the copper content of stream water in Angola (D. J. Atkinson, personal comunication) demonstrated a progressive decline in (a) the metal content, (b) the diurnal variation and (c) the contrast between anomalous and background values from maxima at the start of the rains to minima in the dry season.

TABLE VIII

DISPERSION OF COPPER IN SWAMP SOILS AND STREAM SEDIMENTS DOWN-DRAINAGE FROM A COPPER MINERALIZATION, NORTHERN RHODESIA

Remarks	Distance drown-drainage from mineralization (ft.)	Minus 80-mesh		Minus 200-mesh	
		Total Cu ppm	Readily soluble Cu ppm	Total Cu ppm	Readily soluble Cu ppm
	-300	90	12		
	-100	250	100		
	0	4,500	1,100		
Dispersion down-drainage in seasonal swamp soil	1,000	1,700	800		
	2,000	800	325		
	4,000	600	90		
	5,000	475	120		
	5,500	750	200		
Dispersion train in the active sediment of the outflow stream from the swamp	5,700	750	120	750	145
	6,000	400	40	450	110
	6,500	160	12	250	100
	7,000	440	35	700	180
	8,000	120	25	400	130
	10,000	110	15	275	70
[Confluence with main stream]					
	12,000	55	6	135	30
	13,000	50	8	160	50
Backgound copper content in the sediment of streams draining barren (or feebbly mineralized ?) ground		55	4	105	14
		40	4	105	24
		50	5	95	22

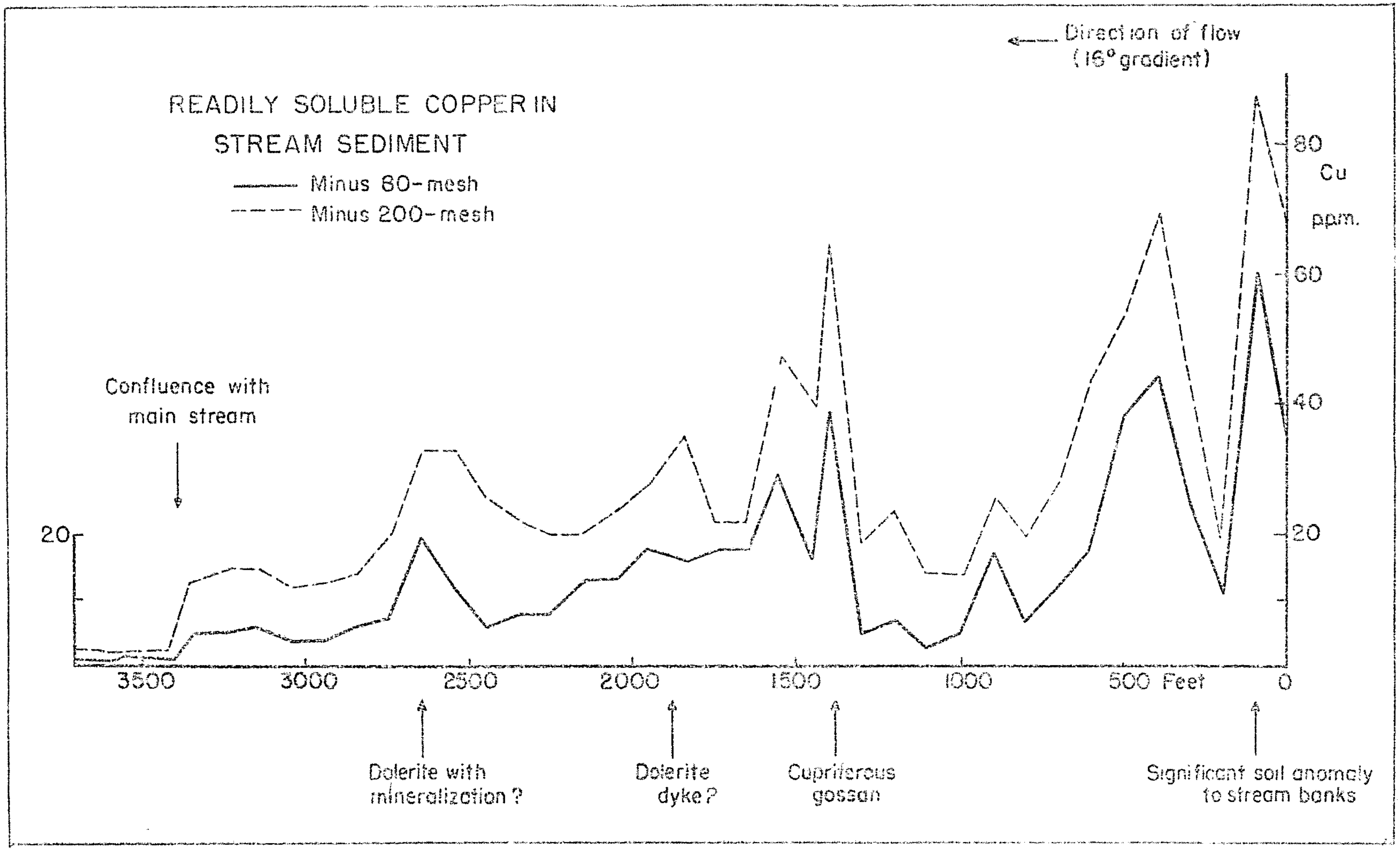

FIGURE 7.-METAL CONTENT OF THE ACTIVE SEDIMENT IN A STREAM DRAINING COPPER MINERALIZATION IN UGANDA.

The results of these studies support the view that the best time of year for water surveys is the period following the early rains, while surface flow remains active and rising groundwater conditions are more constant. It is also evident from the results of the above investigations, and also from a limited number of samples taken in copper-bearing areas in Northern Rhodesia and Uganda, that a more discriminatory field test is required for the reliable detection of significant variations in copper within the range 0.0001 to 0.01 ppm Cu.

Significant metal dispersion trains have also been detected in the sediment of streams and swamps draining mineralized areas in a number of areas in Africa.[5]

Preliminary examinations in Northern Rhodesia have shown that the organic-rich soils of swamps in the vicinity of mineralization often contain abnormally high amounts of cooper and cobalt. The pattern of metal distribution indicates that the metals are precipitated from groundwaters draining deposits situated some thousands of feet away from the swamp (Fig. 2). A high proportion - up to 80 per cent - of the total metal content is readily soluble and very marked contrast between anomalous and barren swamp soils can be obtained by simple, rapid, cold-extraction analysis for copper (Table I(b), see also Figs. 1(a) and 2). The test employed is similar to that previously developed for heavy metals.

Streams usually rise in these "headwater" swamps and anomalous metal contents may continue in the stream sediment for several thousands of feet downstream (Table VIII). Anomalous copper is also detected in the corresponding alluvial bank soils, but the distribution is there more erratic than in the sediments and values decrease away from the present stream channel. Recent work has shown a complex relationship between the metal content of the water and the sediment in the same stream. It seems probable that this relationship is influenced to a large extent by pH, the paths followed by groundwaters before joining the stream, and by the action of bacteria which flourish under tropical conditions. The extent to which these factors and their seasonal variations may affect the interpretation of systematic geochemical data remains to be investigated.

As previously mentioned, the above results refer to drainage dispersions in an area of peneplain topography. By contrast, investigations in the Ruwenzori Mountains in *Uganda* have shown that the detectable train of dispersed copper in the stream sediments downstream from mineralization is shorter (Fig. 7),

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[5] The writer wishes to acknowledge his indebtedness to Dr. H. E. Hawkes and Mr. H. Bloom for information given in advance of publication concerning the results of their experiments with stream sediment sampling in base-metal areas in North America, which are an important contribution to geochemical prospecting technique.

despite the mountainous terrain and the absence of major swamps such as those which restrict metal dispersion in Rhodesia. The reason lies, no doubt, in the fact that erosion is so active that (a) oxidation and leaching extend only to shallow depths, (b) the sediment is kept moving at a high rate, and (c) the stream banks are essentially composed of the neighbouring valley-slope soil. Anomalous sediments are largely eroded anomalous soils, and only part of the metal has been absorbed from metal bearing surface water. Downstream from mineralization, therefore, the metal content of anomalous sediment is rapidly diluted as it descends, by the incorporation of "barren" bank material.

Comparison of the results obtained in Northern Rhodesia and Uganda clearly shows that the balance between topographic relief and the rates of oxidation, leaching and erosion is a critical one. Furthermore, in areas where leaching is effective, the physical and chemical environment, through which the metal-bearing waters move, also constitutes an important factor in determining the form of the metal dispersion pattern. Thus, longer sediment "trains" can be expected (a) in Rhodesia, if streams receive metal-bearing waters that have not passed through an organic-rich swamp; and (b) in Uganda, if less steeply graded streams drain areas of relatively deeply oxidized ore.

The distribution of total and readily soluble metal in Uganda and Rhodesian sediments is given in Table IX. These data show a number of significant differences which cannot be discussed in this short paper but which illustrate (a) the greater effectiveness of determining the readily soluble metal content as compared to total metal and (b) some of the variations which can be expected as a result of changes in conditions of environment.

CONCLUSIONS

1—In residual soil areas, geochemical soil surveys can generally be expected to give reliable indications of sub-outcropping mineralization despite the deep overburden and intense leaching commonly encountered under tropical conditions. This conclusion has been demonstrated for copper-cobalt, lead-zinc, arsenic-antimony (gold ores) tungsten and molybdenum, and is probably also true for tin, niobium and chromium.

Geochemical soil data may also be useful as an aid to geological mapping, particularly in distinguishing between acid and basic bedrock.

2—Although some instances are known where lead-zinc and copper mineralizations can be detected by near-surface soil analysis in areas of transported or colluvial overburden, not enough data is yet available to draw any general conclusions regarding the efficacy of geochemical methods under these conditions.

TABLE IX (a)

COPPER CONTENT AND PARTICLE SIZE IN STREAM SEDIMENTS, NORTHERN RHODESIA

Size-fraction (B.S.S. mesh)	Weight per cent		Total copper			Readily soluble copper		
	Sample B	Sample A	B Background sediment ppm	A Anomalous sediment ppm	Contrast A/B	B Background sediment ppm	A Anomalous sediment ppm	Contrast A/B
— 20+ 35	5.4	24.1	80	180	2.3	8	80	10.0
— 35+ 80	64.4	43.5	40	160	4.0	2	35	17.5
— 80+135	21.1	21.4	40	210	5.2	3	70	23.3
—135+200	5.4	4.6	80	250	3.1	12	110	9.2
—200	1.7	0.6	110	360	3.3	22	170	7.7
— 80			50	220	4.4	4	80	20.0

NOTE: The copper contents for size-fractions below 135 mesh in Sample B are probably rather higher than "average background".

TABLE IX (b)

COPPER CONTENT OF DIFFERENT SIZE-FRACTIONS OF STREAM SEDIMENTS, RUWENZORI MOUNTAINS, UGANDA

Size-fraction (B.S.S. mesh)	Weight per cent		Total copper			Readily soluble copper		
	Sample B	Sample A	B Background sediment ppm	A Anomalous sediment ppm	Contrast A/B	B Background sediment ppm	A Anomalous sediment ppm	Contrast A/B
— 20+ 35	27.7	23.0	30	100	3.3	0.2	5	25
— 35+ 80	26.6	13.8	30	150	5.0	0.4	9	22
— 80+135	9.8	7.8	30	210	7.0	0.4	16	40
—135+200	4.8	5.0	40	260	6.5	0.6	30	50
—200	3.0	2.8	90	500	5.5	2.5	55	22
— 80			45	280	6.2	0.8	28	35

3—In every area so far examined, soil analysis has proved superior to plant analysis.

4—Preliminary studies of copper dispersion in swamp soils and stream sediments, using simple methods of analysis, strongly support the view that these methods, judicially combined with water analysis, have a considerable potential application in regional mineral reconnaissance.

5—Topography, bedrock lithology, the composition, type and maturity of the soil, the presence of organic matter, activity of the biochemical cycle and pH have all been noted as modifying influences in the development of metal dispersion patterns in soil. Metal dispersion in stream sediments and water is also influenced by many of the above factors and, in particular, by the critical balance between the relative rates of leaching and erosion, the maturity of the drainage system, seasonal climatic changes, accumulation of organic matter and pH. The role of bacteria, though probably important, remains to be investigated.

Groups of the above mentioned factors are usually intricately inter-related and stem from local features of the geology, geomorphology and climate.

6—Standard geochemical methods of analysis have been found generally satisfactory for field use under tropical conditions, but in almost every area, some degree of modification has been necessary to meet fully the requirements of the local problem.

7—The complexity and variable influence of the many factors influencing metal dispersion patterns and the choice of methods for detecting them, emphasize the importance of comprehensive field and analytical orientation as essential prerequisites in any new application of geochemical surveys and in the interpretation of their results.

8—Outstanding problems for future investigation include (a) metal dispersion in colluvial soils, (b) further evaluation of the controls influencing metal dispersion in drainage systems and the significance of this dispersion in terms of mineral reconnaissance, and (c) the investigation of methods aimed at delimiting regional geochemical provinces.

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GEOCHEMICAL PROSPECTING IN PERMAFROST REGIONS OF YUKON, CANADA

R. W. Boyle * *

ABSTRACT

Four areas have been tested in the Yukon to determine the applicability of geochemical prospecting methods where permafrost is present. The areas differ geologically and contain deposits of four different types.

The Keno Hill-Galena Hill area contains lead-zinc-silver lodes in quartzites, schists, and greenstone lenses. The area is underlain by permafrost. A detailed hydrogeochemical survey of springs and streams using zinc as an indicator showed that the mineralized belt could be outlined. Several anomalies were found in virgin territory suggesting the presence of undiscovered deposits, Analyses of residual soils using lead as an indicator were effective for tracing the faults in which the lodes occur and to outline the lodes. Analyses of glacial soils and till samples near the surface were not effective for tracing faults or locating lodes, but analyses of glacial material sampled near bedrock gave fair results. Biogeochemical surveys conducted lodes overlain by glacial till showed that certain plants contain more zinc in the vicinity of the lodes, but few anomalies with significant contrast were obtained.

The Vangorda Creek area contains zinc-lead deposits in quartzite, sericite schist, and graphite schist. The area is underlain by permafrost. Springs and streams in the area contain high concentrations of zinc, and hydrogeochemical prospecting methods have been. found to be applicable in the area. Soil analyses have also been found to be effective in outlining mineralized zones.

The Quill Creek area contains nickel-copper deposits in basic and ultrabasic rocks. Permafrost is generally present. A hydrogeochemical survey of the stream draining the area in which the principal deposit occurs showed that the deposit coul be located by following the copper in the water to its source in an outcrop of the deposit in the rocks walls of the stream.

The Whitehorse area contains copper deposits in skarn zones at the contact of granodiorite and limestone. Permafrost is absent in this area except at high elevations. A hydrogeochemical survey of streams draining the copper belt was unsuccessful in outlining the mineralized area because copper is relatively immobile in the area, and zinc is absent in the water.

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INTRODUCTION

The Geological Survey of Canada has recently conducted research on geochemical prospecting with a view to extending the various methods to areas underlain by permafrost. The geochemical investigations included analyses of stream and spring water, residual and glacial soils, till, and gravel for lead, zinc, and copper using dithizone (diphenylthiocarbazone) as reagent. Geochemical work has been done in three areas differing geologically and containing metal deposits of three different types. Most of the research work was carried out in the Keno Hill-Galena Hill area, but limited investigations were also made in the Quill Creek, and Whitehorse areas (See Figure 1).

Two private mining companies have also done geochemical exploration in the Yukon. United Keno Hill Mines have conducted biogeochemical surveys in the Keno Hill area and Prospectors Airways Company Limited has done both soil and water surveys in the Vangorda Creek area. The results of these investigations are summarized in the sections to follow.

KENO HILL-GALENA HILL AREA

TOPOGRAPHY, GENERAL GEOLOGY, AND CLIMATE

The detailed investigations carried out by the Geological Survey in this area are covered by five reports (Boyle, R. W., C. T. Illsley and R. N. Green, 1955a, 1955b; Boyle, R. W., 1956; Boyle, R. W. *et al.*, 1956, in press). In this paper limited space will allow only a brief summary of the result obtained.

The Keno Hill-Galena Hill area is in central Yukon, thirty-five miles northeast of Mayo and some 220 miles due north of Whitehorse. The present economic interest in the area centres chiefly about the lead-zinc-silver deposits which have been worked since 1915 and have produced more than $ 75,000,000 in silver, lead, zinc, and cadmium. The present producing mines in the area are the Hector-Calumet Mine operated by United Keno Hill Mines Limited and the Mackeno Mine, both situated on Galena Hill. Former producing mines were the Silver King, Elsa, and Bermingham on Galena Hill, the Onek, Ladue-Sadie-Friendship, Lucky Queen, Shamrock, and No. 9 on Keno Hill, and the Bellekeno on Sourdough Hill.

The topography of the area is mountainous with elevations ranging from 2,500 feet to 6,750 feet. Areas above 4,200 feet are flat topped with a rolling hilly topography. South-facing slopes are gentle to moderately steep, whereas north-facing slopes, especially on Keno Hill, are precipitous.

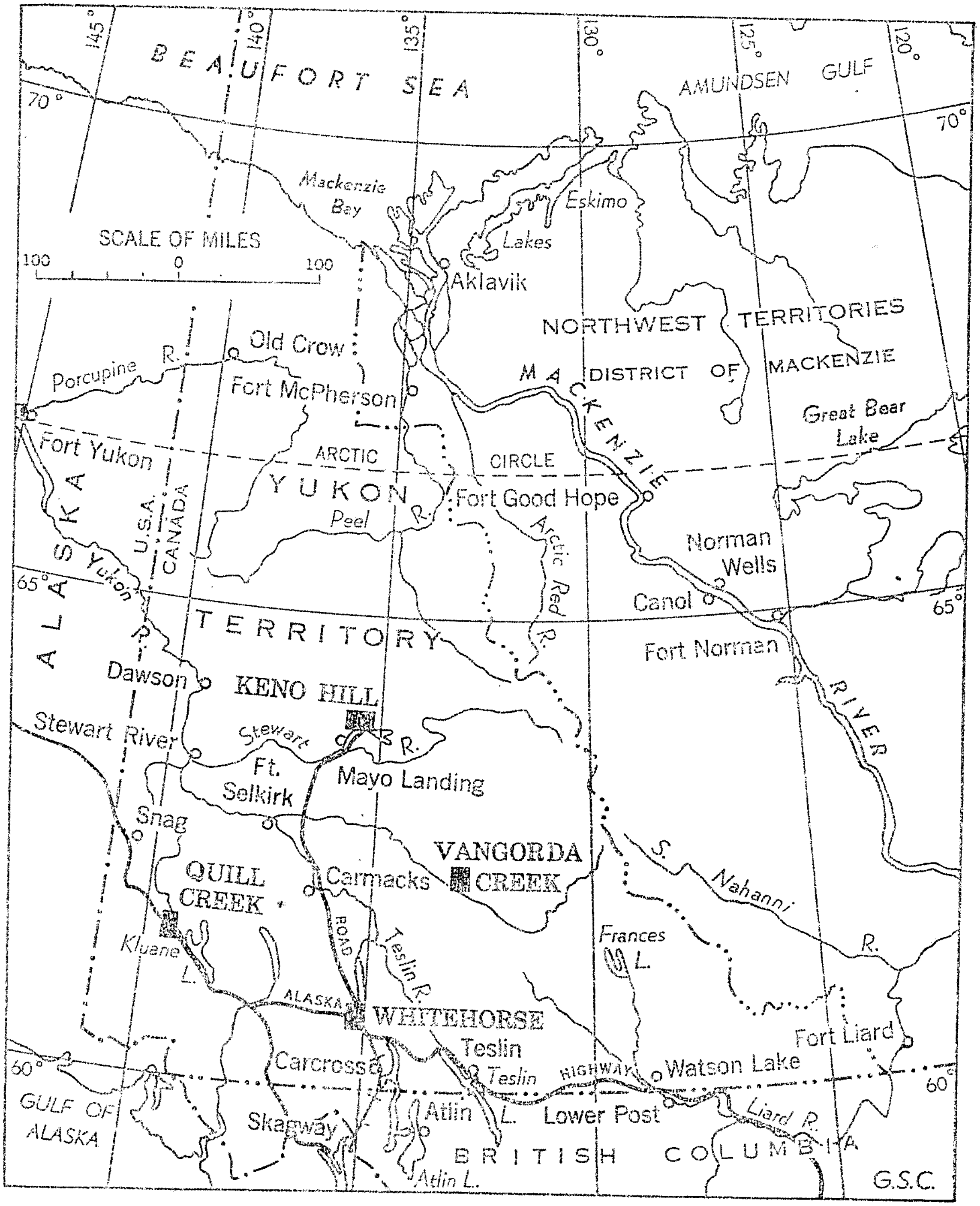

Fig. 1. Index Map showing location of the four areas discussed in the paper.

The consolidated rocks underlying the area belong to the Yukon group and may be Precambrian or Paleozoic in age. They consist of sericitic, chloritic, and graphitic schists, thick-and thin-bedded quartzites, and conformable greenstone sills and lenses. On Keno and Galena Hills the rocks have an average dip of 25 degrees to the south and appear to form the southern limb of a large anticline.

The silver-lead-zinc lodes of the area are localized in brecciated fault zones where these zones intersect thick-bedded quartzites and greenstones. Two types of lodes are recognized; an early type containing quartz, pyrite, arsenopyrite and small amounts of galena and sphalerite, and a late type mineralized with siderite, pyrite, galena, sphalerite, and freibergite. Each type may occur separately, but it is general to find hybrid lodes consisting of the early type which has been fractured and mineralized with minerals characteristic of the late type. The lodes seldom exceed 200 feet in length and 500 feet on the rake; in width they average 3 feet.

Most lodes are oxidized to depths of 250 feet or more. The minerals developed in the oxidized zones include limonite hydrous manganese oxides, calcite, gypsum, anglesite, smithsonite, cerussite, quartz, malachite, and azurite. Much of the oxidation in the veins preceded the formation of the present permafrost, because ice veins occupy the solution channels which were the former courses of underground oxidizing waters. In areas where permafrost is absent and below the lower limit of the permafrost, underground waters are flowing, and oxidation is active at the present time.

In lodes the metallic content of the ore varies with depth, depending upon the extent of oxidation. Unoxidized ore averages about 40 ounces of silver per ton, and contains from 6 to 10 per cent lead, 5 to 9 per cent zinc, and 0.01 to 0.1 per cent copper. Oxidized ore is lower in zinc and generally higher in lead and silver. The silver values range from 60 to 250 ounces or greater per ton, the lead content may increase to 25 per cent or more, and the zinc content may drop to 1 per cent or less. In most lodes the copper content of the oxidized zone remains relatively unchanged from that of the unoxidized zone.

The area was severely glaciated during Pleistocene time, and the terrain below 3,500 feet is covered by a mantle of glacial till and gravel varying in thickness from 10 to 20 feet. Soils developed on the glacial deposits vary from 3 inches to a foot in thickness, exhibit a poorly developed profile, and are characterized by their high organic content. They are very poorly drained and are water-saturated throughout the summer months. Their pH varies from 6.5 to 7.0.

Above the elevation reached in the latest glacial period the soils developed on the bedrocks are predominantly residual, but some intermixed loess and

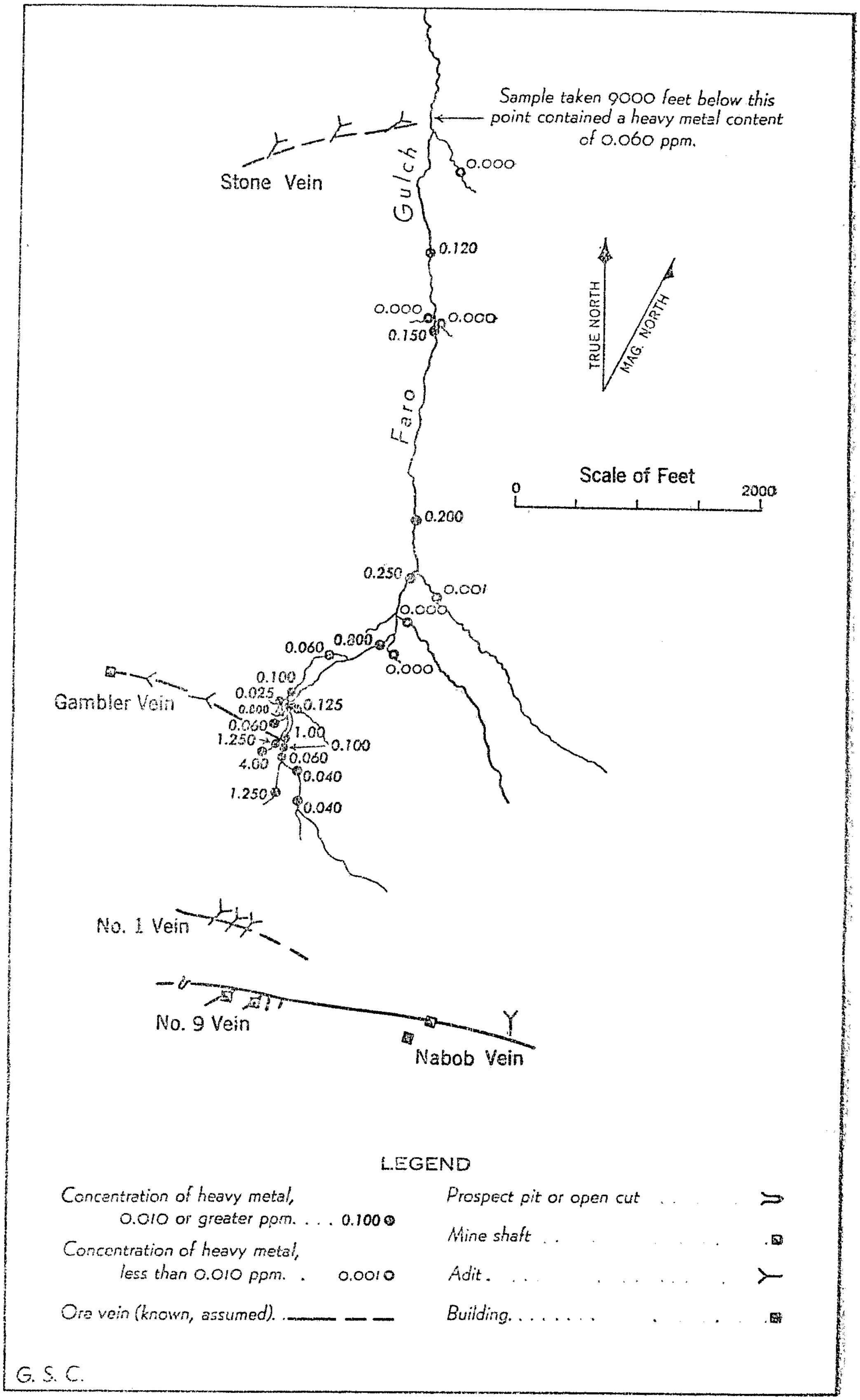

Fig. 2. Heavy metal anomalies in the streams in the Faro Gulch area, Keno Hill, Yukon Territory. An example of anomalies related to known veins and lodes.

decomposed till representing an old glaciation are present in places. The thickness of residual soils is variable, depending upon the slope of the hills. On the tops of the hills soils are seldom more than 3 feet in thickness and may be entirely absent in places. On the lower slopes they are thickened by slope wash and land creep and in places may exceed ten feet in depth. Good profiles are rarely developed, and in most areas the soil has been highly disturbed by frost boiling, which brings rock float, vein material, and bottom soil to the surface. In the areas covered with residual soil and in places in glacial terrain a marked downhill mechanical dispersion of primary and secondary ore minerals and mineralized lode material has been produced by land creep, slope wash, and frost action on steep slopes. The residual type soils are moderately well drained to poorly drained and vary in pH from 5.5 to 6.5.

Although the area is in a region of permanently frozen ground, the permafrost is patchy in its distribution. Factors promoting permafrost include a northern hillside exposure, high elevation, and the presence of a thick insulating layer of moss and muskeg. Flowing surface and underground water thaws the ground, and in many places frost-free strips occur in the vicinity of surface and underground water channels. Frozen ground and ice veins have been encountered in the mines down to depths of 300 feet or more. Below the permafrost, underground water are circulating freely through the lodes and along faults, fractures, and bedding planes.

The climate of the area is rigorous. The mean annual temperature is 26°F, the average minimum 14°F, and the average maximum 37°F. Temperatures as low as —80°F, and as high as 90°F have been recorded. The winters are long and cold with only a few hours daylight each day, and the summers are short and warm with nearly continuous daylight.

The average annual precipitation at Mayo is 11.23 inches. The rainfall in the Keno Hill-Galena Hill area is greater than at Mayo owing to the influence of the high mountains to the north and west. The snowfall is moderate and usually commences in mid-September or early October. Most of the snow has melted by the end of May, but local patches and small snowfields remain in sheltered places on northern slopes until late August.

RESULTS OF GEOCHEMICAL INVESTIGATION IN KENO HILL AREA

STREAMS AND SPRINGS

The streams in the area have two origins; some drain small lakes which act as reservoirs, providing a regular flow throughout the summer months; others are fed by a network of tributaries which derive their water from normal runoff and numerous springs.

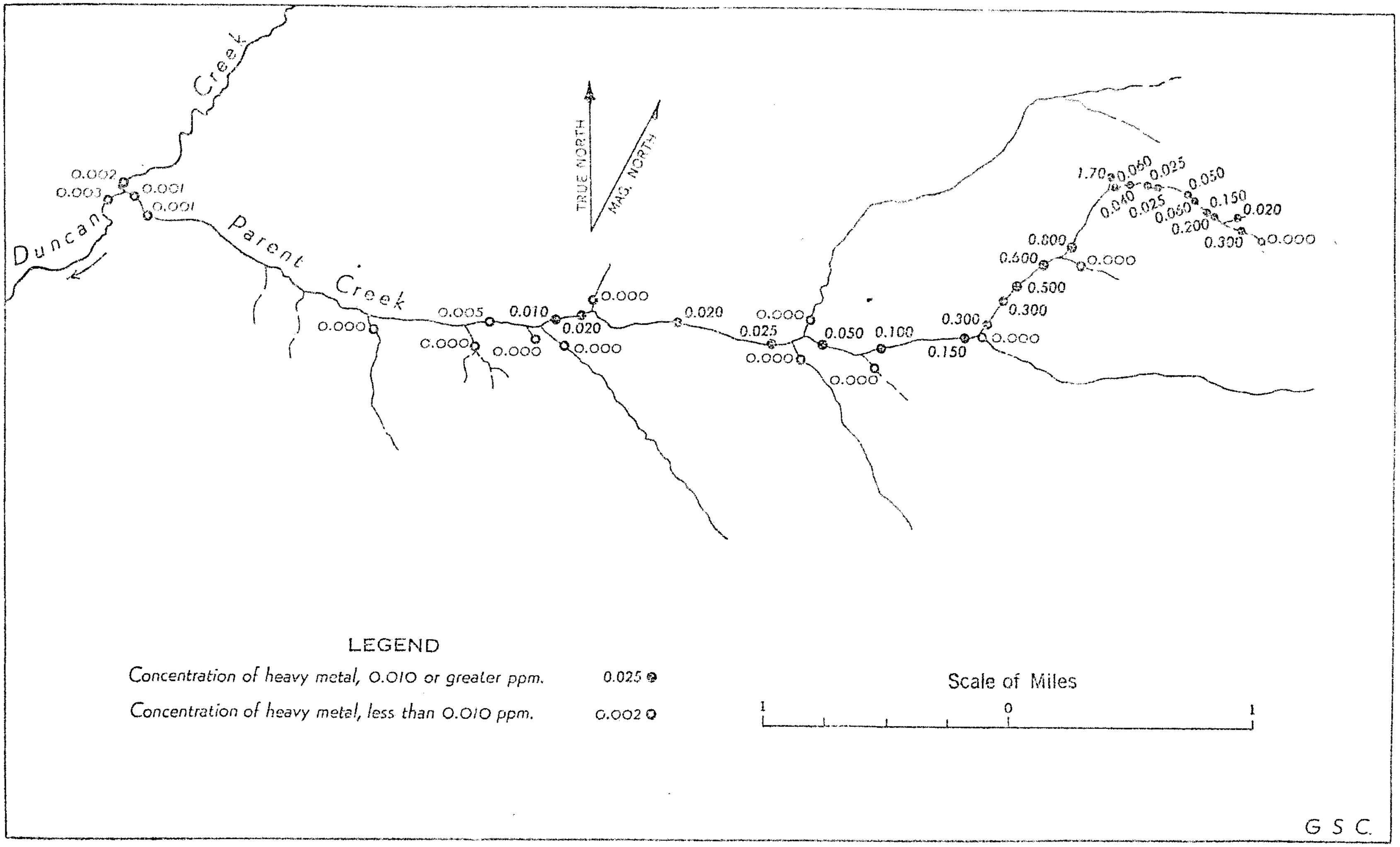

Fig. 3. Heavy metal anomalies in the Parent Creek stream system, Keno Hill area, Yukon Territory. An example of an anomaly in virgin territory.

The springs have several origins. Some, at the heads of tributaries of the main streams, are situated in wet muskeg and drift and consist of a small pool of water fed by seepage from rainwater and the melting of the active layer of the surrounding permafrost. The water in other springs issues from the base of accumulations of rock float and is derived principally from rainwater and the melting of small snowfields and the active layer of the permafrost. This water in some cases percolates through several hundred feet of loose rock which may contain vein float. Certain springs issue from fractures and faults in the underground workings and in the headwalls of gulches and along rock bluffs. These springs are clearly distinguished by their high zinc, iron, manganese, and sulphate content and are marked by red or chocolate coloured precipitates which form at their orifices or the stream bottoms into which they flow. Locally these precipitates cement gravel, rock fragments, and vegetation and form characteristic limonitic conglomerates.

The detailed hydrogeochemical investigation of streams and springs show that zinc is markedly dispersed from the deposits, lead is relatively immobile, and the migration of copper is restricted to a few hundred feet. Other cations dispersed from the deposits in solution include Mg, Ca, Al, Si, Fe, Mn, Ni, Na, K, Cs, Co, and Sr. Sulphate is the principal anion, but carbonate is also present in some springs.

Several zinc anomalies were outlined in the stream systems draining the area underlain by a favourable quartzite formation in which most of the economic lead-zinc-silver loder occur. Some of the anomalies are obviously related to known veins and lodes (Figure 2) ; others occur in virgin territory (Figure 3) and are probably related to deposits that are covered by drift or lie at depth. Two of the anomalous areas in unprospected territory were investigated by private companies by ordinary methods of prospecting and by soil and plant analyses. At the time of writing the results of these investigations have been negative, but work is expected to continue in the area where the anomalies occur.

SOIL ANALYSES

Samples of residual soil, glacial till, and soils developed on till were obtained by hand auger, shovel, and bulldozer along traverse lines across known lodes and vein faults. The results of analyses of these samples show that the zinc content is erratic, owing to its high dispersion by ground and surface water, and that this element is not reliable as an indicator for accurately locating lodes or vein faults. Copper, owing to the general low content in the deposits, is also not a suitable indicator in the soils and till. Lead, however, has a limited chemical dispersion and is enriched in residual soils in the vecinity of the lode deposits, making it an ideal indicator.

The results of analyses of residual soil along traverses across known mineralized vein faults indicate that the lead content of the soil rises several times over the background, and produces an anomaly with a strong contrast over or in the immediate vicinity of the vein faults. Where lead-zinc-silver lodes are present the anomaly is marked and values tens, and in places hundred, of times greater than background occur. Near surface sampling of residual soil is generally effective in tracing vein faults, but where slope wash has produced a thick layer of soil, deep sampling near bedrock is necessary.

Analyses of near-surface glacial soil, till, muck, and peat along traverses across known vein faults are generally unsatisfactory for tracing vein faults or indicating the location of lodes. Samples of glacial material taken a foot or so above the bedrock, however, may give good anomalies with strong contrast over the vein faults and lodes.

BIOGEOCHEMICAL INVESTIGATIONS

Biogeochemical surveys in the Keno Hill-Galena Hill area have been conducted by United Keno Hill mines in an effort to trace vein faults and lodes mainly in areas covered by glacial drift. Twigs and leaves of Labrador Tea (*Ledum* sp.), black spruce (*Picea mariana*) and dwarf birch (*Betula glandulosa*) were sampled along traverses at right angles to known vein faults and in areas where vein faults and lodes were suspected. Zinc is the principal heavy metal concentrated in the plants and served as the indicator element.

The results of the work were inconclusive. The plants in the vicinity of some vein faults and lodes contained slightly higher values in zinc than those over a terrain where mineralization was absent, but anomalies with significant contrast were obtained in only a few places. However, further research is being carried out by United Keno Hill Mines using both soils and plants in an effort to determine the best method of geochemical prospecting for locating new deposits.

WHITEHORSE AREA

The topography of the Whitehorse area is mountainous, and the climate is similar to that at Keno Hill. The general geology has been described by Wheeler (1952).

The area is underlain by Mesozoic limestones and schists of sedimentary origin. These are intruded by granites, diorites, and syenites, all of which are probably related to the Cretaceous Coast Range granites. The youngest rocks are basalts of Tertiary age. Boulder clays and till are concentrated in the main valleys of the area, and the permafrost is patchy and restricted to the higher elevations.

Contact metamorphic copper orebodies, containing bornite, chalcopyrite, tetrahedrite, and chalcocite in lenses and irregular masses of magnetite and hematite, occur in skarn zones at or near the contacts of the limestones and granitic rocks. Sphalerite and pyrite are rare in the deposits. The minerals composing the skarn zones include garnet, pyroxenes, tremolite, epidote, calcite, serpentine and quartz. The main oxidation products of the copper minerals are malachite and azurite. Most of the deposits outcrop or are covered by only a foot or so of soil. Permafrost is absent in the areas containing the copper deposits.

All of the mines of the area have been inactive for many years, and recent exploration along the copper belt has been unrewarding.

The streams draining the copper belt were tested in the spring and fall of 1954 and 1955, but the results were disappointing. No heavy metal anomalies were detected in the streams despite the fact that in two cases the old mine dumps are leached by small streams. In one case an analysis of the water in an open pit on a former copper orebody gave only 0.015 p.p.m. copper.

The reasons for the failure of hydrogeochemistry in the Whitehorse area may be attributed to two factors, the low dispersion of copper in the water draining the area containing the deposits, and the virtual absence of sphalerite in the deposits, resulting in the lack or soluble zinc salts as indicators in the water. The mobility of copper seems to be influenced by the alkaline character of the water which gave consistent pH values of 8 and by the presence of an abundance of limestone. Thus, it would appear that any copper dissolved from the deposits is rapidly precipitated from solution by the limestone to form carbonate (azurite or malachite) and that only small amounts migrate in alkaline waters.

In the Whitehorse area the low dispersion of copper from the deposits suggests that pedogeochemical methods would be applicable in the area, and in certain places analyses of the limestones may be effective for locating lodes because fractures and seams in these rocks are coated with copper stain for several tens of feet away from the lodes.

QUILL CREEK AREA

The Quill Creek area is located 200 miles northwest of Whitehorse on the Alaska Highway. The topography is mountainous and the climate is similar to that at Keno Hill. Permafrost underlies most of the area.

The general geology has been described by Muller (1954). The country rocks are Paleozoic sediments intruded by large peridotite masses with associated gabbro and diorite bodies. The principal ore deposit under active exploration by the Hudson Bay Mining and Exploration Company is a high-grade nickel-copper deposit containing nickeliferous pyrrhotite and chalcopyrite in a shear zone near the contact of a peridotite mass and siliceous sediments. The orebody outcrops on the sides of a small mountain stream forming a tributary of Quill Creek. The surface outcrop is oxidized, and limonite with intermixed malachite are the principal secondary minerals. The outcrop has not been significantly disturbed except for a few small prospect pits.

During the summer of 1955 water samples from Quill Creek and the tributary stream crossing the high-grade orebody were analyzed for copper. The samples taken from Quill Creek contained less than 0.002 p.p.m. copper, but those in the tributary stream contained relatively high copper values, which increased towards the nickel-copper orebody outcropping in the rock walls of the stream. These results indicate that hydrogeochemistry is suitable for locating copper deposits of the Quill Creek type and should be applicable to the long belt of favourable rocks northwest and southeast of Quill Creek.

VANGORDA CREEK AREA

The geology of the Vangorda Creek area and the geochemical methods used in this area have been summarized by Chisholm (1956).

The topography and climate are similar to that at Keno Hill, and permafrost underlies much of the area. The underlying rocks are quartzite, phyllite, sericite schist, and graphitic schist. An orebody consisting of finegrained pyrrhotite and pyrite, containing galena and sphalerite in a siliceous groundmass was discovered in 1953 on Vangorda Creek. Most of the ore zone is covered with a 50-foot deep mantle of glacial drift, and several geophysical methods and a geochemical survey were used by Prospectors Airways Company Limited in a attempt to outline the mineralized zone.

According to Chisholm, electro-magnetic and self-potential methods were first tried but were found to be ineffective owing to the presence of graphitic schist. A magnetometer survey likewise gave unsatisfactory results owing to the erratic distribution of pyrrhotite and the presence of basic intrusive plugs which obscured the picture. The zone was finally outlined by a gravimetric survey and geochemical soil survey.

The geochemical soil survey, using dithizone as reagent, showed a relatively constant heavy metal content over the ore zone but gave distinct anomalies on the low ground on either side owing to the heavy metal content precipitated from down-slope drainage water. The heavy metal content of the water in Vangorda Creek, which cuts through the deposit, also increased significantly as the ore zone was approached, and in the vicinity of the ore zone there are springs precipitating iron compounds and carrying high values in zinc. These features suggest that this deposit could have been easily located by hydrogeochemical methods, and Chisholm has concluded that the best preliminary method of exploration in the Vangorda Creek area is a geochemical reconnaissance, followed by detailed magnetometer, electro-magnetic, and gravity surveys.

CONCLUSIONS

The presence of permafrost in the areas investigated does not seriously affect the application of geochemical methods except in obtaining soil samples. Thus, deep sampling of soils is impossible by hand methods in many cases, and the use of a mechanical drill may be necessary. In residual and some glacial soils frost action is actually an advantage because pieces of vein float and secondary ore minerals have been brought to the surface by frost boiling, and surface samples reflect the presence of buried vein faults and lodes.

Oxidation of the lodes in most cases is not inhibited by permafrost because there are sufficient windows in the permafrost to allow oxidizing waters to enter the veins and faults at higher elevations and to issue at lower elevations with their dissolved heavy metal. In some areas, however, the veins and lodes are sealed by permafrost, and do not yield heavy metals to surface waters. In other areas underlain by permafrost there is usually sufficient thawing near the surface to expose veins and vein float to circulating near-surface waters that carry traces of the heavy metals.

In the Keno Hill are zinc has the highest dispersion of the three elements (Cu, Pb, Zn) detected by the dithizone reaction. Zinc can be detected in many streams miles from its source, and since it is generally abundant in most of the lode deposits of the area it is a good indicator element for tracing mineralizatoin by hydrogeochemical prospecting methods. The high dispersion of zinc may produce erratic values in residual soils and in vegetation, and it is, therefore not suitable as an indicator element in soil and biogeochemical methods for accurately locating vein faults and lodes. Zinc may, however, be useful to indicate the presence of mineralization in a general area.

Lead is relatively immobile and has a limited dispersion from the Keno Hill-Galena Hill deposits. The element is enriched in residual soil in the vicinity of the lead deposits, and it is, therefore, an excellent indicator for locating vein faults and lodes, using soils analyses. Experience shows that it cannot be used in hydrogeochemical methods.

The copper content of the lodes in the Keno Hill area is too low to produce significant anomalies in either the stream system or in the soils, and hence copper cannot be used successfully in any of the geochemical methods.

The hydrogeochemical investigations in the Keno Hill-Galena Hill area indicate that most of the heavy metal anomalies in the stream systems are restricted to a belt centered on the area underlain by a favourable quartzite formation in which most of the important lead-zinc-silver deposits occur. This evidence suggests that hydrogeochemical prospecting is suitable for outlining the extent of mineralized belts in the Yukon and hence should isolate the area in which the prospector can concentrate his efforts to find deposits by means of ordinary prospecting techniques, geophysical methods, and biogeochemical methods and soil analyses.

Some of the anomalies found in the streams of the Keno Hill area are undoubtedly due to oxidation of old mine dumps and mines, but a large part of the geochemical research was carried out in areas where mining activity is absent; several significant anomalies were found. In view of this it seems highly probable that the mineralized belt of the Keno Hill and Galena Hill area could have been outlined by hydrogeochemical methods before any of the deposits were disturbed.

Analyses of residual soils in the Keno Hill area using lead as indicator show that it is possible to trace vein faults and locate lead-zinc-silver lodes. Analyses of glacial soils and till sampled near the surface are not effective in tracing vein faults or locating lodes, but analyses of glacial material a foot or so above bedrock yield better results.

Both soils and water analyses are effective methods of geochemical exploration in the Vangorda Creek area and may be used in conjunction with geophysical methods.

Hydrogeochemical methods do not appear to be applicable to copper deposits of the Whitehorse type owing, it is thought, to the precipitating effect of limestone on the copper. On the other hand, water analyeses may be a valuable exploration method in locating copper-nickel deposits in the Quill Creek area.

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METAL CONTENT OF MINE WATERS

W. H. Brown * and R. B. Fulton * *

ABSTRACT

Data are presented regarding the pH and the metal content of mine water, plotted for the gallons per minute pumped from the Austinville, Virginia, mine and from the recently unwatered Arminius mine at Mineral, Virginia. At Austinville a lead-zinc deposit in lower Cambrian dolomite is being mined. Data for this property cover a six year period. At Mineral, a massive sulphide orebody in metamorphic rocks was mined during the period 1890 to 1918 when the mine was allowed to fill with water. Dewatering started in late 1954 and was completed in about a year. Pumpage from this mine is now equivalent to the natural inflow. The acid mine water pumped from the remnants of massive sulphide ore at Mineral has a high metal content whereas the alkaline water pumped from the disseminated lead-zinc deposit at Austinville has a low metal content.

INTRODUCTION

Work in soil prospecting for zinc in recent years has shown very definitely that geochemical anomalies can be divided into two types; residual anomalies and dispersion anomalies. The formation of the latter involves solution, transportation and redeposition of the soil zinc. Since mine waters most nearly represent the type which could accomplish this transportation; a study of mine waters is in order.

Analytical data on mine water from two different types of mines in Virginia are presented, showing pH of the mine waters, their metal content and the gallonage pumped. One case is the Austinville mine where sphalerite, galena and pyrite mineralization occur disseminated in dolomite. The other is the Arminius mine where sphalerite, galena and less commonly chalco-pyrite are constituents of a massive pyrite body in sericite quartzite.

CASE I

The Austinville mine of The New Jersey Zinc Company, located in Wythe County in southwestern Virginia, lies in the valley of the New River in the Ap-

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palachian Valley and Ridge physiographic province. The mine is within a few hundred feet of the river and its lowest level is about 900 feet below the surface of the river. The country rock is fractured and faulted limestone and dolomite with numerous solution cavities. Fluorescein dyeing of the river and its tributaries demonstrates that some surfaces water flows into the mine. One tributary has been flumed to minimize its contribution to the mine.

The mine has been kept unwatered by continuous pumping for about 30 years. The accompanying pumping record for the period 1950 to 1956 indicates the rate that is required to keep the mine dewatered.

Quarterly tests of the water pumped from the mine are made to determine its content of zinc, lead, copper, and iron, and its pH. Results of zinc, lead, copper and pH determinations are reported for the period from the first quarter of 1950 through the first quarter of 1956. Iron is reported from the first quarter of 1954 onward. Table I lists these data and Figure 1 shows them in graph form. Median values for the metals and pH are:

pH	8.2
Zinc	0.10 ppm
Lead	0.03 ppm
Copper	nil
Iron	3.2 ppm.

Lead and zinc, the ore metals, occur as sulphides which replace the dolomite and fill fractures in it. Oxidation of the sulphides produces lead and zinc silicates and carbonates in overlying soils, mainly at the soil-rock interface. The occurrence of the soil zinc in the district has been studied by Fulton (1950). The sulphide ore bodies contain some pyrite and locally have pronounced pyritic roots. Mineral zoning in the mine is described by Brown (1935). Mining has reached the pyritic roots in places.

CASE II

The Arminius mine is located in the Virginia Piedmont in Louisa County near the headwaters of a small tributary of the North Anna River. The lowest level of the mine is about 1000 feet below the small creek's surface. Country rocks are metamorphic sericite quartzite, chlorite amphibole quartzite and feldspathic chlorite biotite schist, impermeable rocks which do not permit ready deep circulation of surface waters.

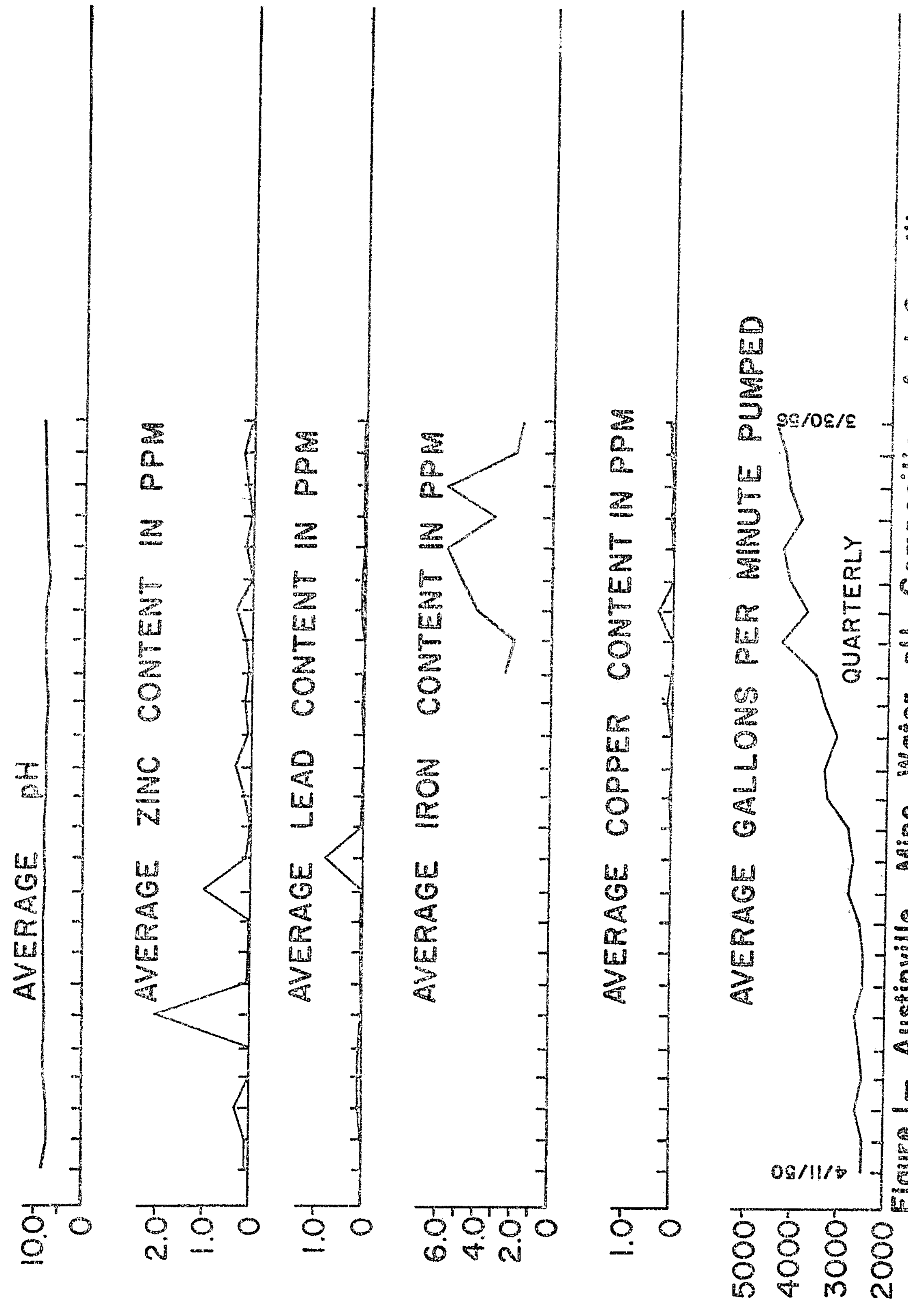

Figure I — Austinville Mine Water- pH, Composition And Quantity

Main production of the mine was pyrite during the period 1890 to 1918 The mine was allowed by the last operators to fill with water in the early 1920's. The New Jersey Zinc Company started dewatering operations in December 1954, completing them in September 1955, and since then has maintained the dewatered condition. The accompanying pumping record indicates the rate during the dewatering process and the markedly lower rate to keep it dewatered, the latter essentially being equal to the rate of inflow.

For a time, daily tests were made of pH, combined zinc-lead-copper content and iron content of the mine water. Combined zinc-lead-copper is determined by a dithizone titration at pH 8.3, and the value is reported as zinc equivalent. Frequency of the metal tests was reduced later to two tests per week and finally

TABLE I

AUSTINVILLE MINE

Date	pH	PPM Zn	PPM Pb	PPM Cu	PPM Fe	Pumping rate Gallons/minute
4/11/50	8.4	0.10	nil	nil		2450
7/1/50	7.8	0.10	nil	nil		2450
10/7/50	7.7	0.35	0.04	nil		2600
12/16/50	8.2	nil	0.06	nil		2450
3/31/51	8.2	nil	0.05	nil		2550
6/21/51	8.0	2.0	0.01	nil		2650
9/25/51	8.2	0.04	nil	nil		2450
12/29/51	8.3	tr	0.005	nil		2450
3/27/52	8.3	tr	0.05	nil		2550
6/30/52	8.0	1.0	0.05	nil		2800
9/27/52	8.1	0.10	0.80	nil		2690
12/22/52	8.3	nil	tr	nil		2800
3/13/53	8.0	8.16	0.03	0.005		3250
7/2/53	8.1	0.35	nil	nil		3350
9/29/53	8.1	0.1	nil	nil		3090
12/28/53	7.9	0.19	0.01	0.10		3390
4/1/54	8.1	0.10	nil	nil	2.4	3575
6/29/54	8.2	0.16	tr	nil	2.0	4025
10/1/54	8.3	0.35	0.07	0.30	4.0	3750
12/30/54	7.5	nil	0.09	nil	4.8	4100
4/1/55	8.2	8 18	nil	nil	5.6	4250
7/6/55	8.2	tr	0.05	0.05	3.2	3890
10/10/55	8.4	0.11	0.02	nil	5.6	4150
12/30/55	8.5	0.21	0.04	0.08	2.00	4225
3/30/56	8.8	0.05	0.04	0.08	1.60	4440

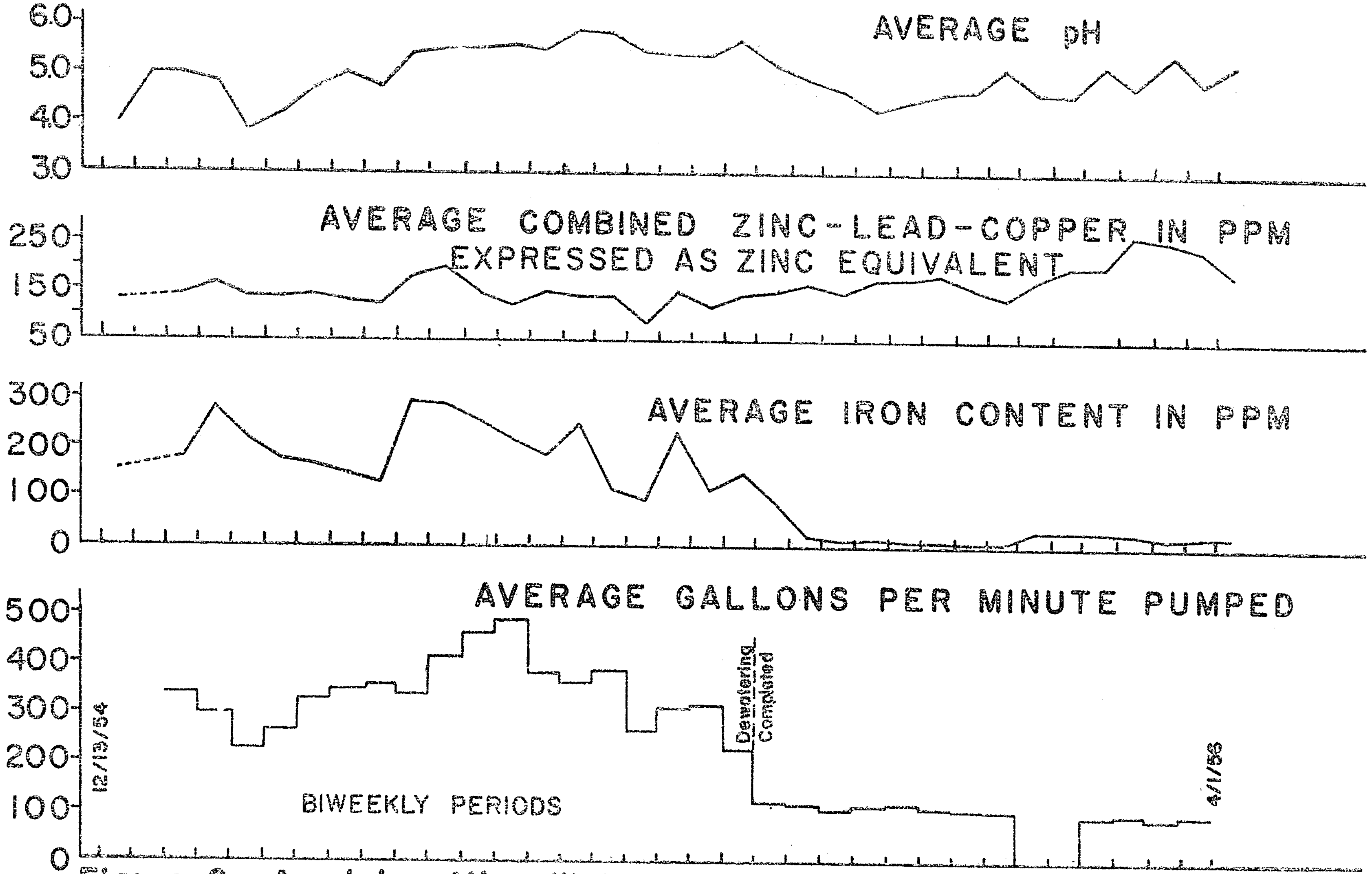

Figure 2 – Arminius Mine Water-pH, Composition And Quantity

to one per week. Determination of pH has been kept on a daily basis. Because of the variation in frequency of testing, results are listed as biweekly averages in Table II, and these values are used in the graphic presentation in Figure 2. Median values determined from all of the biweekly averages are:

pH	5.0
Zinc-lead-copper	146 ppm (expressed as zinc equivalent)
Iron	114 ppm

Median values of biweekly averages since the mine was dewatered are:

pH	4.8
Zinc-lead-copper	172 ppm
Iron	21 ppm

The ore mineralization is massive pyrite with disseminated sphalerite, galena and less common chalcopyrite. The pyrite body is in sericite quartzite. Some carbonate is present as calcite or ankerite, but the volume is relatively small. The sulphides weather to form a gossan cap which has a zone of typical copper enrichment beneath it.

The present shaft is inclined under the ore with its collar about 100 feet in the footwall. There is a pronounced dripping of water into the shaft at the soil-rock interface which is actually gradational, making a drip zone in the shaft several feet thick at about 150 feet below the collar. At this zone metal rungs on the shaft ladders are dissolving by action of the dripping water, a phenomenon not observable elsewhere in the shaft. Observation of water flow in ditches on the several levels shows the 200' level to be wettest, with water obviously running in from old stopes which extended nearly to the surface.

COMPARISON OF CASES I AND II

Case I is in predominantly limestone and dolomite terrain whereas Case II is in an area of relatively little carbonate. In the former case pyrite occurs disseminated and as fracture fillings; in the latter it forms a large, massive body many times the former in concentration. Lead and zinc content of the ore bodies in the two cases are within a few percent of each other.

The rate of pumping required to keep the mine in limestone unwatered is about thirty-five times that required for the mine in metamorphics. This is a reflection of the degree of natural underflow of water in the two terrains. The former area is in a large valley next to a major river. The latter is at the head-

TABLE II

ARMINIUS MINE

Biweekly Periods	pH	PPM Zn *	PPM Fe	Pumping rate Gallons/minute
Dewatering operation				
12/13/54—12/25/54	4.0	130	154	00
12/25/54—1/8/55	5.0	—	—	—
1/9/55—1/22/55	5.0	142	180	338
1/23/55—2/5/55	4.8	165	281	298
2/6/55—2/19/55	3.9	135	218	227.6
2/20/55—3/5/55	4.2	134	176	265
3/6/55—3/19/55	4.7	140	165	326
3/20/55—4/2/55	5.0	129	147	348
4/4/55—4/16/55	4.7	121	129	356
4/17/55—4/30/55	5.4	173	292	337
5/1/55—5/14/55	5.5	186	288	414
5/15/55—5/28/55	5.5	144	253	461
5/29/55—6/11/55	5.6	120	216	485
6/12/55—6/25/55	5.5	146	183	380
6/26/55—7/9/55	5.9	136	250	362
7/10/55—7/23/55	5.8	138	114	386.5
7/24/55—8/6/55	5.5	88	94	266
8/7/55—8/20/55	5.4	147	232	312
8/21/55—9/3/55	5.4	113	116	316
9/4/55—9/17/55	5.7	141	149	227
Dewatering completed				
8/18/55—10/1/55	5 2	148	85	120.6
10/2/55—10/15/55	4.9	163	21	119.8
10/16/55—10/29/55	4.7	146	12	108.5
10/30/55—11/12/55	4.3	171	18	113.6
11/13/55—11/26/55	4.5	172	11	118.3
11/27/55—12/10/55	4.6	184	11	110.8
12/11/55—12/24/55	4.7	152	7	108.8
12/25/55—1/7/56	5.1	133	7.5	106
1/8/56—1/21/56	4.7	170	31.2	
1/22/56—2/4/56	4.6	200	30.5	
2/5/56—2/18/56	5.2	204	31	94
2/19/56—3/3/56	4.8	263	26.1	97
3/4/56—3/17/56	5 4	252.5	18	91
3/18/56—3/31/56	4.9	235.5	23.1	96
4/1/56—4/14/56	5.2	186	24.6	95

* Combined zinc-lead-copper are expressed as zinc equivalent.

waters of a small creek near a divide several miles away from the nearest river. The former is in relatively soluble limestone-dolomite rocks where solution cavities are common; the latter is in relatively insoluble siliceous rock which is highly impermeable.

Median values of pH and metal content of the mine waters are compared below:

	CASE I	CASE II (since dewatering)
pH	8.2	4.8
Zinc	0.10 ppm	
Lead	0.03 ppm	
Copper	nil	
Combined zinc-lead-copper	0.13 ppm	172 ppm
Iron	3.2 ppm	21 ppm

Mine water in Case I is alkaline; in Case II it is acid. Zinc-lead-copper content of Case II is 1000 times that of Case I. Iron content of Case II is seven times Case I.

CONCLUSIONS

The two cases cited show a marked difference in the pH and metal content of the mine waters. Decomposition of the sulphides in the limestone-dolomite terrain of Case I does not result in an acid water. The acid character of their oxidation product is ameliorated by reaction with the enclosing carbonate rock and with its natural alkaline waters. The massive sulphides of Case II oxidize to produce acid waters which are not sufficiently neutralized by the minor carbonate present to raise their pH to the alkaline range.

This relationship of sulphides in dolomite resulting in alkaline mine waters and sulphides in schist resulting in acid waters is not universally true. In The New Jersey Zinc Mine at Gilman, Colorado deposits of massive sulphides in dolomite have very acid minewaters. It is believed that the presence of massive iron sulphides at Mineral and Gilman is responsible for producing the acid mine waters.

The outstanding conclusion is that acid waters of Case II carry many times the amount of heavy metals in solution than the alkaline waters of Case I. This is attributed mainly to the greater solubility of the metals in acid water; though the greater volume of water flowing through the mine in Case I would also tend to produce smaller concentration through its greater dilution.

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II—GEOCHEMICAL AND BIOGEOCHEMICAL METHODS OF PROSPECTING

БИОГЕОХИМИЧЕСКИЙ МЕТОД ПОИСКОВ И РАЗВЕДКИ РУД

А. П. Виноградов и Д. П. Малюга

ABSTRACT

1—The biogeochemical methods of prospecting for ore are based on a knowledge of the normal chemical concentration of an element in soils and plants. The chief guide in prospecting for ore is the increasing content of the chemical element in plants, then the formation of peculiar biocoenoses within certain soil-climatic zones, the appearance of plant-concentrators, and finally, the appearance of a morphological variability among the local vegetation.

2—The chief migration pattern, which is dependent on the hydrogeological and soil-climatic conditions of the territory, is considered for the chemical elements over the mineralized zone.

3—The sampling technique and the field methods of analysis are described.

4—The results are given for biogeochemical prospecting for nickel, cobalt, copper, lead, zinc, molybdenum, chromium, and other elements in the southern part of the Ural Mountains, the Transbaikal, the Caucasus, and other territories of the USSR.

5—Comparisons are made between the biogeochemical methods in ore search and prospecting and the metallometric survey, the hydrochemical method, and other water halo methods. The possible depth of bedding disclosed by the biogeochemical methods is discussed, and the faults and the advantages of the methods are given.

I—ОСНОВАНИЯ

Поиски руды по содержанию того или иного химического элемента в почвах или в растениях, произрастающих над рудой, основываются на хорошо и давно известных многочисленных фактах значительной концентрации в этих случаях почвами и растениями рудных элементов. Можно различать два основных типа растений-концентраторов. Первый тип концентраторов – это когда все растения данной местности с повышенным содержанием того или другого химического элемента в почвах, породах концентрируют его в той или иной степени и в растительных тканях. Второй вид концентраторов – видовой (или родовой), когда только определенный вид (или род) селективно среди всех других видов данного растительного сообщества исключительно высоко концентрирует данный элемент.

Можно напомнить в этом отношении виды цинковой, литиевой, алюминиевой и др. аналогичных флор (Виноградов, 1938, 1949).

Но влияние высокой концентрации в среде того или другого химического элемента на растения не ограничивается только высоким содержанием в данных растениях этого химического элемента. Влияние на растения в этих случаях значительно многообразнее. В районах рудных месторождений нередко можно наблюдать своеобразный подбор и распределение растений, появление характерных местных растительных биоценозов и типичных растений – концентраторов. Затем появление внешней морфологической изменчивости местных видов растений, появление их морф, подвидов, физиологических рас, "привыкших" к влиянию рудного элемента и т.п. Мы можем в качестве иллюстрации продемонстрировать два вида Linosyris villosa L. и Pulsatilla patens L. Mill. и ряд других видов, которые на перидотитовых массивах с месторождением Ni на Южном и Среднем Урале дают своеобразные морфы, являющиеся растениями-индикаторами (Труды Биогеох, 1932-1954).

Подобных примеров можно было бы привести достаточно много (Виноградов, 1954; Труды Биогеох, 1932, 1954). Таким образом при биогеохимических поисках руд мы обращаем внимание на химическую экологию (Виноградов, 1949, 1954).

Области, где наблюдается подобная биологическая реакция растительного (и животного) покрова вследствие влияния избыточного (или недостаточного) содержания в почвах и породах того или иного химического элемента, мы называем биогеохимическими провинциями. В пределах этих провинций обычно наблюдаются биогеохимические эндемические изменения флоры (и фауны) и даже их заболевания.

Поэтому при поисках биогеохимическим методом мы не ограничиваемся опробованием растений (и почв) на содержание в них того или иного химического элемента, а пользуемся всей совокупностью поведения флоры данной провинции. В этом, прежде всего, отличие биогеохимического метода поисков руды от металлометрической съемки.

Систематическое изучение состава растений и разных почв и их отдельных горизонтов, а также изучение подвижности ионов различных химических элементов в биосфере показало нам, что поиски биогеохимическим методом могут быть с успехом использованы для Ni, Co, Cu, Cr, Mo и др. месторождений и не представляют практического значения для ряда других элементов. Последнее относится к очень распространенным элементам, например, Mg, Si и т.д., и к тем элементам, которые в условиях биосферы, как правило, не дают истинных (ионных) растворов – например, Zr, Th, Ti и др. и, поэтому, не усваиваются растениями. Наиболее эффективные результаты дает биогеохимический метод поисков месторождений Se, Cr, Co, Ni, Cu, Zr, Mo, Ag, Sn, Au, Pb, U, Hg и др., вследствие образования ими легкоподвижных простых и комплексных ионов.

Разные растения и разные их части – корни, ветви, листья и т.п. нередко по разному накапливают тот или иной химический элемент. Поэтому, требуется некоторое предварительное исследование, выяснение наиболее характерных проб частей растений. Как общее правило – растения с интенсивным водообменом и с глубокими корнями являются наилучшим материалом. Обычно мы пользовались зеленой частью травянистой растительности, или листьями, хвоей деревьев. Нередко в зоне растений концентрация рудного элемента значительно выше, чем в местной почве.

Как будет видно дальше, накопление того или иного химического элемента в растениях и почвах идет параллельно. В зависимости от типа почв, наибольшая концентрация нередко наблюдается в одном из почвенных горизонтов. Нам приходилось производить определения в разных зональных типах почв – подзолистых, каштановых, черноземных, бурых лесных, сероземных и субтропических желтоземах и кремнеземах (Виноградов, 1952; Малюга, 1956 г.)

На этих примерах мы останавливаемся ниже. Но, как правило, можно сказать, что почвы аридных областей – почвы сероземные, бурые, частично каштановые и др. почвы сухих степей мало промываются. Поэтому вынос из верхних почвенных горизонтов мало выражен и опробование можно вести в верхнем слое, обычно мощностью ок. 15-20 см.

Почвы черноземные промываются больше, но не дают резкого различия в распределении отдельных химических элементов по вертикальному профилю и поэтому мы берем пробу из верхнего, сильно гумусированного горизонта.

Что касается почв из области гумидного климата, в частности, подзолистых почв, серых и бурых лесных почв, и южных желтоземов – то вследствие интенсивного промывания верхние (негумусированные) горизонты могут быть обеднены, а наоборот, горизонт вмывания – иллювиальный обогащен многими химическими элементами. Поэтому, пробу почв следует в этом случае брать и из горизонта вмывания (иллювиального). Действительно, не только на Южном Урале, но и в Туве, на Кавказе нами было обнаружено, что ореол рассеяния рудных месторождений Co, Ni, Cu, Mo, Cr, U и др. особенно чувствуется при анализе проб из верхнего гумусированного горизонта почв и в иллювиальном горизонте, тогда как промежуточные почвенные горизонты этих почв обеднены металлами вследствие выноса метеорными водами и интенсивного извлечения их корнями растений.

II—МИГРАЦИЯ ХИМИЧЕСКИХ ЭЛЕМЕНТОВ НАД ЗОНОЙ ОРУДЕНЕНИЯ

Причиной повышенного содержания рудных элементов в почвах и растениях являются ореолы рассеяния вокруг рудных тел и месторождений.

Обычно различают первичные и вторичные ореолы рассеяния. Первые связаны с гипогенными процессами, причем проникновение в этих случаях рудных элементов по вмещающие породы и образование ореолов рассеяния, как хорошо известно, не велико.

Наиболее обширны вторичные ореолы рассеяния – напр. в зоне окисления рудных месторождений. Форма ореола рассеяния зависит от многих причин – глубины залегания жилы, мощности прикрывающих рудные тела древних наносов, почв, гидрогеологических условий местности, ее рельефа и т.д.

Механический способ рассеяния (снос) нередко играет существенную роль. На него накладываются химические и биогеохимические процессы, вызывающие миграцию тех или других элементов в виде растворов и газов. При благоприятных геологических и климатических условиях растворы проникают в трещиноватые и пористые породы и достигают поверхности. Подобного рода ореолы рассеяния мы обнаружили в районах никелевых и хромовых месторождений на Южном Урале и др. что описывается далее. Обширные ореолы рассеяния дают те химические элементы, ионы которых наиболее подвижны в условиях биосферы и особенно те из них, которые образуют вторичные месторождения, напр. UO_2^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Cu, Se и др. Геохимическое поведение отдельных элементов или их пар Ni/Co, Zn/Cd, Th/U и т.п. в зоне гипергенеза является основным для поисков руды биогеохимическим методом.

Однако, надо помнить, что подвижность отдельных ионов и химических соединений в биосфере контролируется очень многими физико-химическими факторами t°, pH, red/oxy, органическим веществом и т.д. Различные сочетания этих условий усложняют картину миграции отдельных химических элементов в пределах рыхлых осадочных пород биосферы.

III—ОТБОР ПРОБ И ПОЛЕВЫЕ МЕТОДЫ АНАЛИЗА

Наиболее благоприятны для применения биогеохимического метода поисков руды – области со спокойным рельефом – плато, долины, пологие склоны гор и холмов, покрытые современными древними осадками.

Метод предполагает предварительное общее знакомство с геологией, гидрогеологией, климатом, почвами и флорой района. Затем производят рекогносцировочное опробование почв и растений. Берется 2-3 профиля почв и растительного покрова. Участок, подлежащий полному опробованию, разбивается прямоугольной сеткой, которая наносится на карту масштаба 1:10000. Проводятся параллельные линии отбора проб (вдоль предположительных жил или линий разлома и т.п.), обычно в расстоянии 100-200 м друг от друга. Отбор проб производится через 5-20 метров. Пробы почв берутся по почвенным горизонтам. Характер проб растительности определяется предварительным опробованием (листья, ветви, корни и т.п.). Для полевых определений были использованы химические методы, полярографические и спектральные (Малюга, 1954; Виноградов, 1952; Труды Биогеох, 1932-1954).

IV—ОСНОВНЫЕ РЕЗУЛЬТАТЫ ПОИСКОВ РУДЫ БИОГЕОХИМИЧЕСКИМ МЕТОДОМ

За последние годы биогеохимический метод был нами испытан в разных условиях в трех районах Советского Союзана Среднем и Южном Урале, в Туве и на Кавказе для поисков U, Ni, Co, Cu, Cr, Pb, Zn, Mo и др. руд. В настоящей работе освещаются главным образом исследования, произведенные на Южном Урале и в Туве.

Южно-Уральский рудный район представляет исключительное практическое значение. Здесь находятся Кемпирсайские никелевые (силикаты Ni) месторождения, затем хромитовые, медистые. Многие из этих месторождений хорошо разведаны буровыми скважинами. Поэтому здесь возможна была корреляция между данными биогеохимического метода и разбуривания. Были обследованы Н. Тайкеткенское, Чугаевское и Промежуточное никелевые месторождения в пределах Кемпирсайского рудного поля, затем Викторовское хромитовое месторождение (Донское) и месторождения меди Ю. Юлук и Бакр-Узяк (район Сибая).

1—*Кемпирсайское рудное поле*

Месторождения приурочены к древней коре выветривания Кемпирсайского перидотитового массива. Размытая поверхность выветривания серпентинитов и неизмененные породы прикрыты пестроцветными глинами и мергелями различной мощности, от одного до 15 м. Район месторождений приподнят до 420-450 м над уровнем моря. Грунтовые воды находятся на глубине 20-30 метров от поверхности, иногда ниже залегания руды. Ультраосновные породы часто перекрыты габбро-амфиболитами, почти полностью обохренными или каолинизированными. Присутствие более стойких и менее стойких пород нарушает сплошное залегание рудного тела, из-за чего образовались карманообразные залежи руды различной мощности. В сложении Кемпирсайских никелевых месторождений принимают участие осадочные отложения мелового и третичного возраста – пестроцветные глины, мергели и пески. Чередуясь с габбровыми охрами и выщелоченными серпентинитами они являются породами, из которых образовался почвенный покров – темнокаштановые, каштановые солонцеватые и другие почвы.

Растительный покров в пределах рудного поля более разряжен, чем вне рудных участков. Среди растительности встречаются этиолированные растения (Salvia dumertorum, Galatella punctata и др.).

Обращают внимание многочисленные варианты морфы Pulsatilla patens (L.) Mill. с разной окраской цветов и разной формой листьев и т.п. (рис. 1, 2, 3).

Исключительно сильные изменения морфы происходят на никелевых месторождениях у Linosyris villosa. Это растение широко распространено в южноуральских степях, составляя 1-10% растительного покрова ковыльно типчаковой степи (рис. 4).

Изменение формы растений вместе с тем содержат очень высокие количества Ni, а также Co и Cu. Из табл. 1 видна степень обогащения почв и растений, произрастающих над месторождениями.

Таблица 1

Содержание Ni, Co и Cu в нормальных растениях и их морфах, с месторождений Ni (% золы)

Название вида		Ni	Co	Cu
Anemone patens	(нормальная)	$7{,}8 \cdot 10^{-4}$	$2{,}6 \cdot 10^{-4}$	$1{,}3 \cdot 10^{-3}$
” ”	(морфа с Ni-месторождения)	$3{,}1 \cdot 10^{-2}$	$1{,}2 \cdot 10^{-3}$	$1 \cdot 10^{-2}$
Linosyris villosa	(нормальная)	$1 \cdot 10^{-3}$	—	—
” ”	(морфа с Ni-месторождения)	$2{,}2 \cdot 10^{-2}$	$2{,}6 \cdot 10^{-3}$	$1{,}0 \cdot 10^{-2}$
Pulsatilla patens	(нормальная)	$6 \cdot 10^{-4}$	—	—
” ”	(морфа, белая, с Ni-месторождения)	$3{,}7 \cdot 10^{-2}$	—	—
Pulsatilla patens	(морфа, уродливая, с Ni-месторождения)	$2{,}5 \cdot 10^{-2}$	—	—

Рис. 1—Нормальная форма *Pulsatilla patens* (L.) Mill.

Рис. 2—Переходная форма *P. patens*.

Рис. 3—Редуцированная, безлепестковая форма *P. patens*.

Рис. 4—Linosyris villosa L. Левая – нормальная форма; правая – редуцированная форма.

Таблица 2

Распределение кобальта, никеля и меди по горизонтам в почвах Н. Тайкеткенского никелевого месторождения

Почва и ее происхождение	Горизонт и его глубина в см	Содержание в сухой почве, %			Ni:Co	Ni:Cu	Кларк концентрации *		
		кобальт	никель	медь			Co	Ni	Cu
Светлокаштановая, солонцеватая, суглинистая с габбро-амфиболитов, разрез № 22 вне рудного поля	A 0–10	$3{,}0 \cdot 10^{-3}$	$1{,}3 \cdot 10^{-2}$	$3{,}0 \cdot 10^{-3}$	4,3	4,3	3	3	3
	B 10–30	$3{,}7 \cdot 10^{-3}$	$1{,}3 \cdot 10^{-2}$	$9{,}0 \cdot 10^{-3}$	3,5	1,4	4	3	4
	C 30–40	$3{,}0 \cdot 10^{-3}$	$1{,}4 \cdot 10^{-2}$	$7{,}6 \cdot 10^{-3}$	4,7	1,8	3	4	4
Солонец обыкновенный, суглинистый, в 3 м от рудного поля, разрез 13	A 0–10	$6{,}8 \cdot 10^{-3}$	$5{,}7 \cdot 10^{-2}$	$9{,}6 \cdot 10^{-3}$	10	6	6	14	5
	A 35-45	$3{,}9 \cdot 10^{-3}$	$5{,}7 \cdot 10^{-2}$	$6{,}0 \cdot 10^{-3}$	14	10	4	14	3
	B 45–55	$4{,}0 \cdot 10^{-3}$	$5{,}7 \cdot 10^{-2}$	$6{,}2 \cdot 10^{-3}$	14	9	4	14	3
Темнокаштановая суглинистая с рудного поля, разрез № 14	A 0–17	$2{,}3 \cdot 10^{-2}$	$3{,}5 \cdot 10^{-1}$	$1{,}0 \cdot 10^{-2}$	15,2	35	23	90	5
	B 17–34	$1{,}2 \cdot 10^{-2}$	$2{,}6 \cdot 10^{-1}$	$6{,}4 \cdot 10^{-3}$	12,5	40	12	60	3
	C 34–44	$5{,}8 \cdot 10^{-3}$	$1{,}2\ 10^{-1}$	$3{,}0 \cdot 10^{-3}$	20	40	6	30	2

* Среднее содержание никеля в обычных почвах $4{,}0 \cdot 10^{-3}$%, кобальта – $1{,}0 \cdot 10^{-3}$%, меди – $2{,}0 \cdot 10^{-3}$%.

а) *Ново-Тайкеткенское никелевое месторождение*

Приурочено к Кемпирсайскому перидотитовому массиву и находится в северной части Актюбинской области. Район преимущественно сложен серпентинитами. Ультраосновные породы во многих местах перекрыты габброамфиболитами, которые сплошь обохрены или каолинизированы. На этих породах образованы почвы. Руда залегает на глубине 10-15 м. Грунтовые воды проходят на глубине 10-30 м ниже залегания руды. Благодаря высокой проницаемости пород существует постоянная связь с почвенным

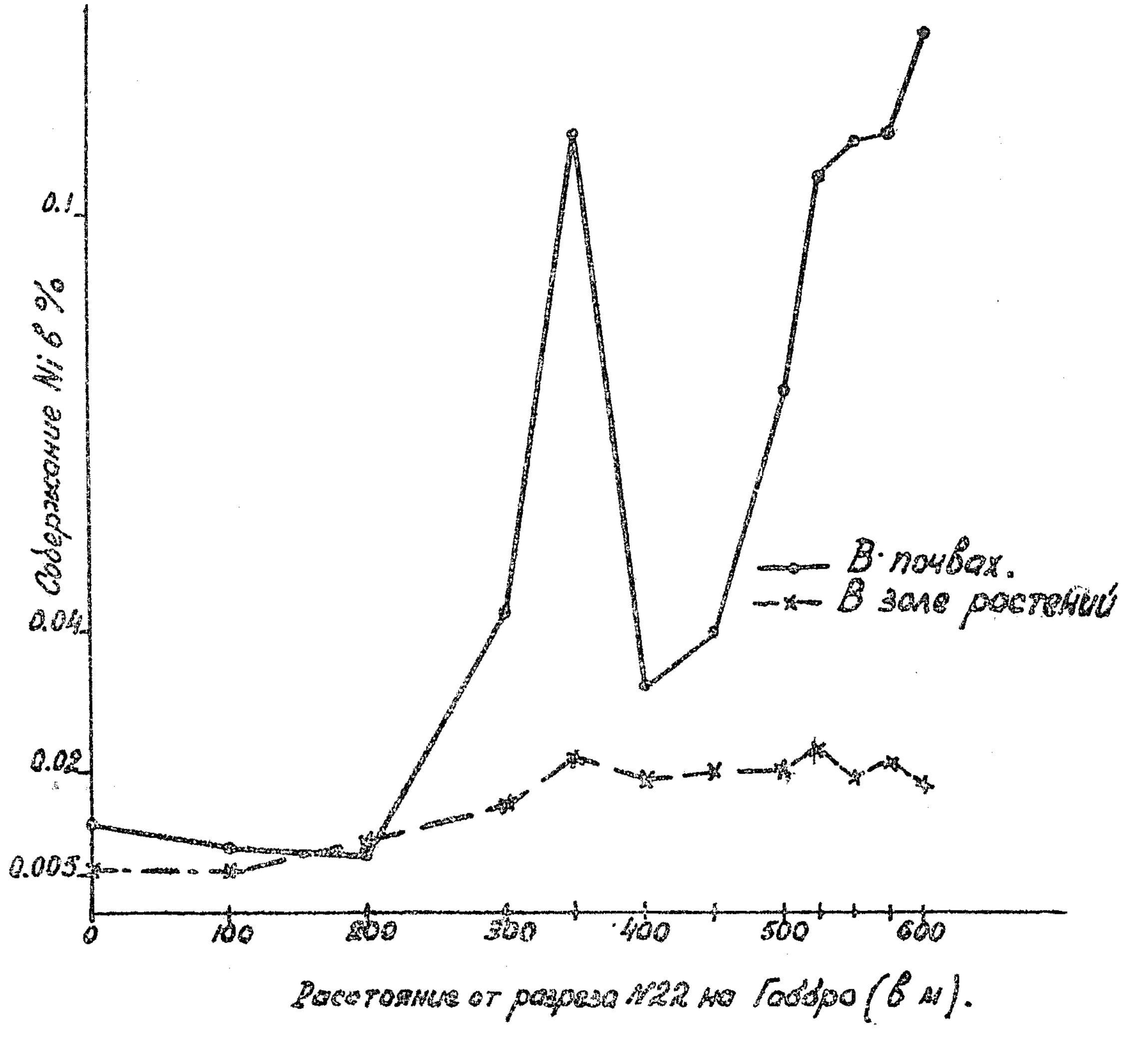

Рис. 5—Содержание Ni в почвах и растениях (золе). Н. Тайкеткенского месторождения.

слоем за счет капиллярного поднятия растворов. По профилю почв происходит накопление Ni, Co, Cu а также и в растениях.

В результате многочисленных определений Ni, Co и Cu в почвах и растениях этого района выяснилось, что содержание Ni, Co и Cu в растениях повышается параллельно повышению их содержания в почвах (рис. 5).

Затем весьма важным признаком наличия никелевого месторождения явилось отношение Ni/Co, достигавшее до 20-27, как в почвах, так и в золе растений. Это отношение Ni/Co ~ 20 относится к никелевым рудам, связанным с ультраосновными породами. В другом случае, о чем мы говорим ниже (месторождения Тувы), отношения Ni/Co иные. Таким образом, соотношение пар близких элементов при биогеохимических поисках имеет также существенное значение для прогнозирования.

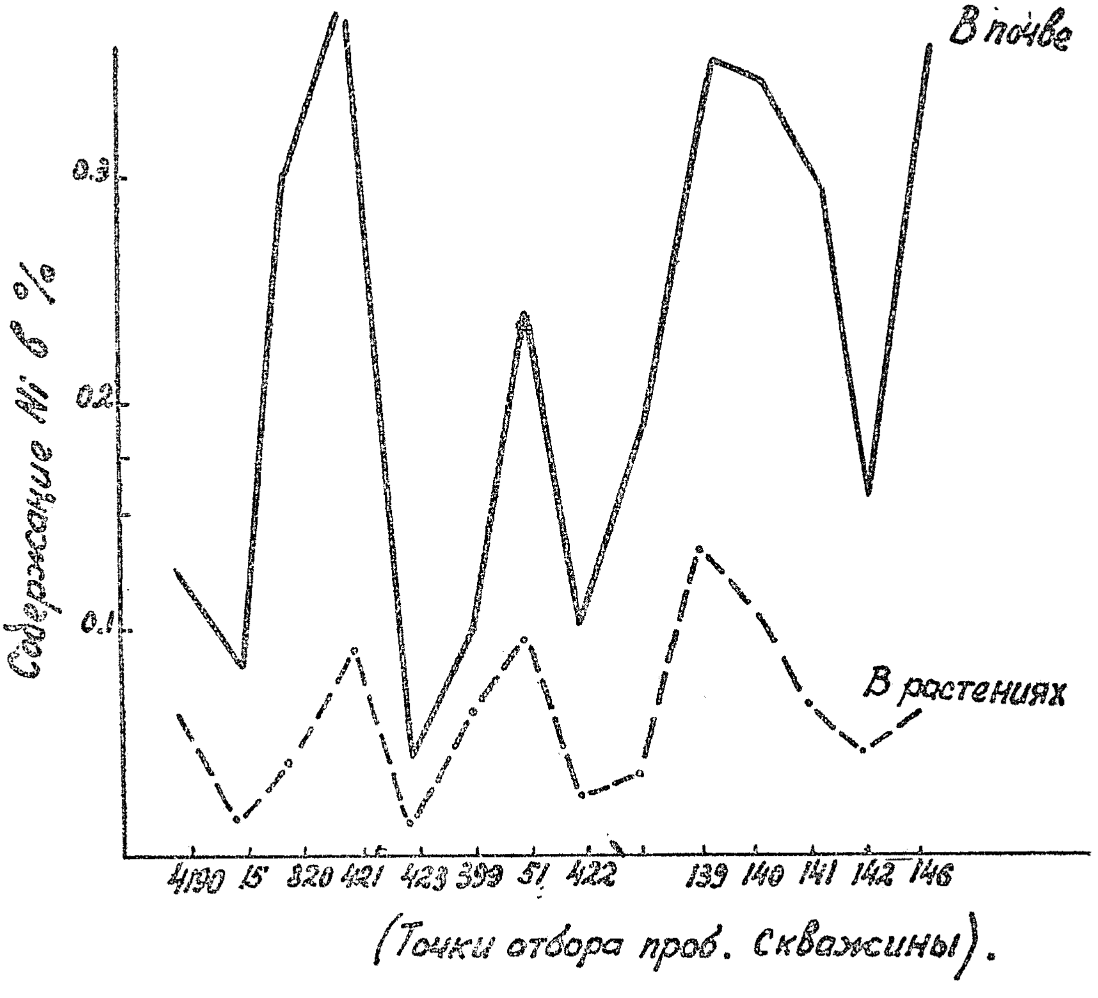

Рис. 6—Содержание Ni в почвах и растениях (зола). Чугаевского месторождения.

б) *Чугаевское никелевое месторождение*

По своему характеру район месторождения близко напоминает Ново-Тайкеткенский. Растительный покров содержал в своем составе виды, морфологически измененные. Они имели высокое содержание Ni и др. металлов. Содержание Ni в почвах и растениях в этом районе также хорошо коррелировалось (рис. 6).

На основе многочисленных определений были составлены карты распределения в этом районе Ni, Co, Cu как в почвах, так и растениях (рис. 7).

Отношение Ni/Co для почв колеблется от 9 до 26 (в среднем ок. 20), а в растениях (Linosyris villosa) от 4 до 16 (в среднем ок. 12) (рис. 8, 9).

Из данных по содержанию Cu в золе растений также следовало, что отношение Ni/Cu изменялось в сторону большего относительно содержания в растениях Cu по сравнению с почвами (в среднем, в почвах Ni/Cu ~ 20, а в растениях Ni/Cu ~ 3).

Опыты по извлечению из местных почв различными растворителями (H_2O, 2% HCl, 5% NH_4Cl) Ni, Co, Cu показал большую извлекаемость Cu,

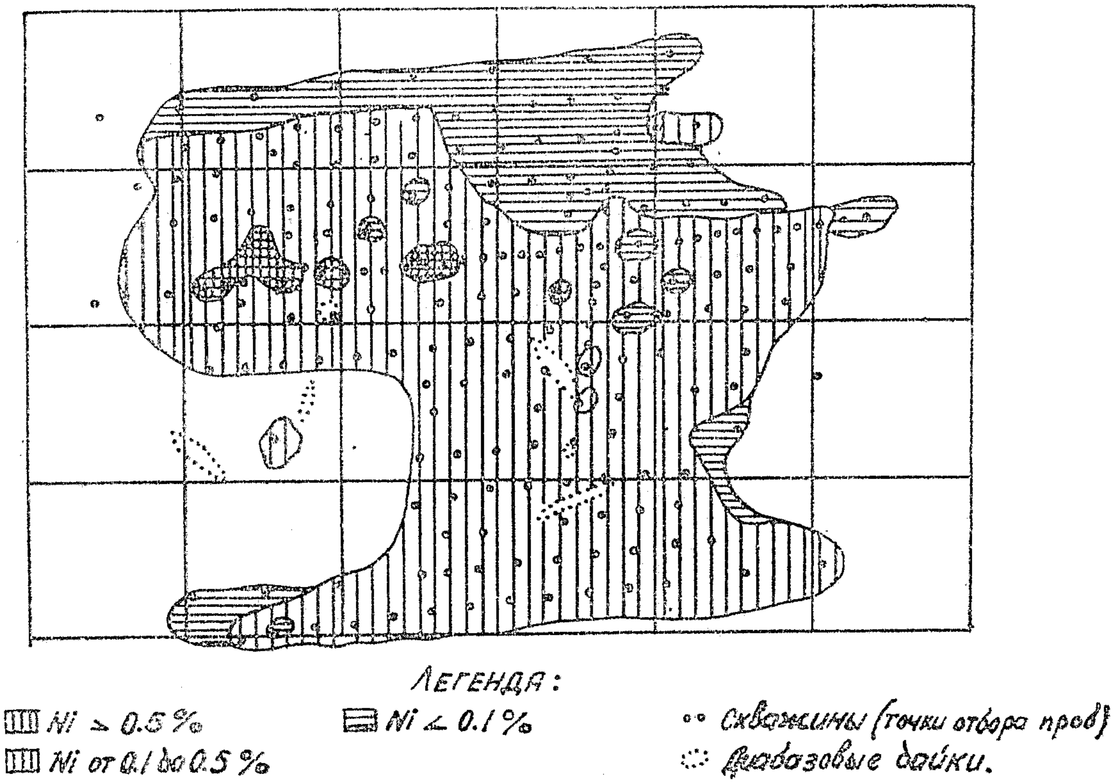

Рис. 7—Распределение Ni в почвах Чугаевского месторождения.

затем Co и меньше других Ni (0,01% от общего его содержания в почвах). Все это вместе указывает на большую подвижность Cu и Co и более прочную фиксацию почвами и породами Ni. Растения в свою очередь относительно больше накапливают Cu и Co, чем Ni.

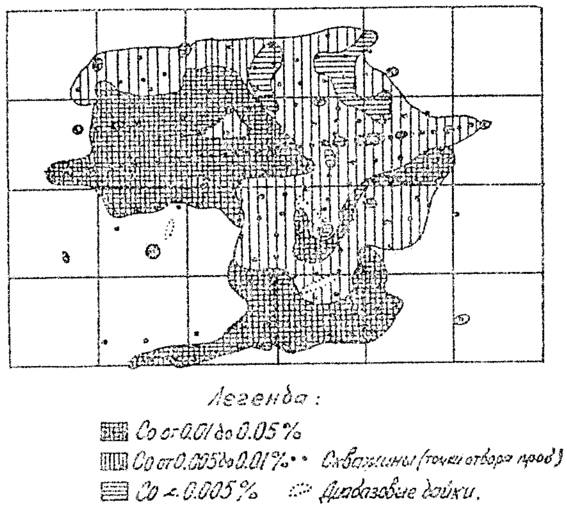

Рис. 8—Распределение Co в почвах Чугаевского месторождения.

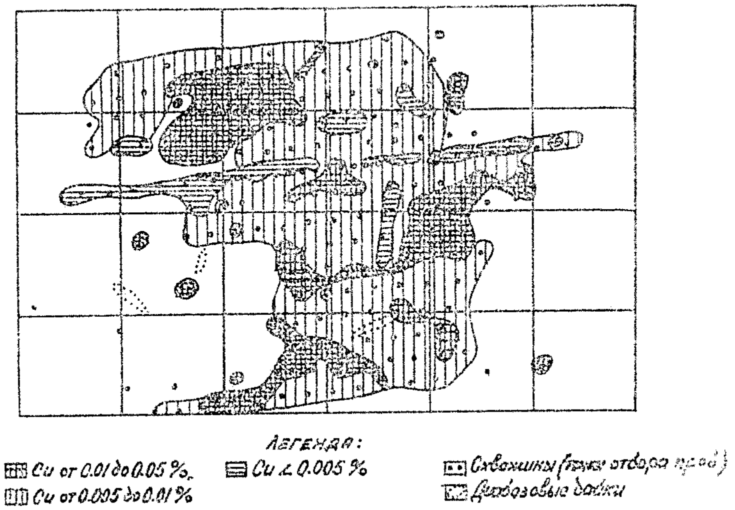

Рис. 9—Распределение Cu в почвах Чугаевского месторождения.

в) *Промежуточное и Кемпирсайское (Бугор) никелевые месторождения*

Были обследованы перспективные площади. Однако рекогносцировочные пробы указали в среднем на низкое содержание Ni в почвах

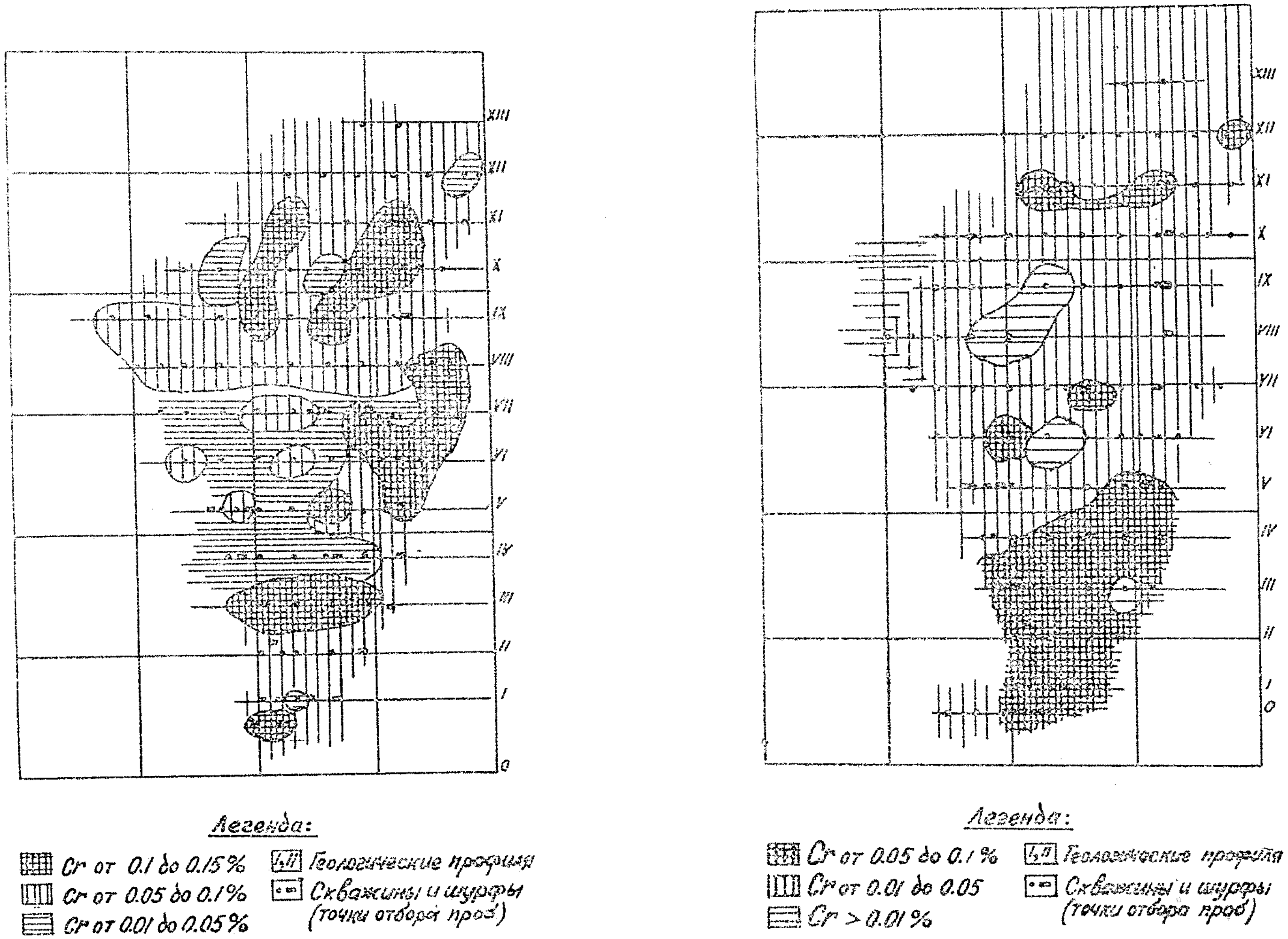

Рис. 10—Распределение Cr в почвах Викторовского месторождения.
Рис. 11—Распределение Cr в растениях (золе) с Викторовского месторождения.

($5 \cdot 10^{-2}\%$). Составленная карта содержания Ni, Co, Cu на этих площадях указывала на отсутствие промышленных руд, что и было подтверждено бурением.

2—*Викторовское хромитовое месторождение*

Относится к хромитовому району Южного Урала (Актюбинская обл., "Донское"). Происхождение хромитовых руд связано с наличием здесь богатых хромом дунитовых серпентинитов, почти на всей площади прикрытых слоем мезозойских отложений. Мезозойские осадочные породы (суглинки, глины) и выщелоченные серпентиниты являются вмещающей толщей блоков плотного почти неизмененного хромита. Месторождение имеет совершенно гладкую поверхность. Сплошной покров каштановых почв прочно закреплен

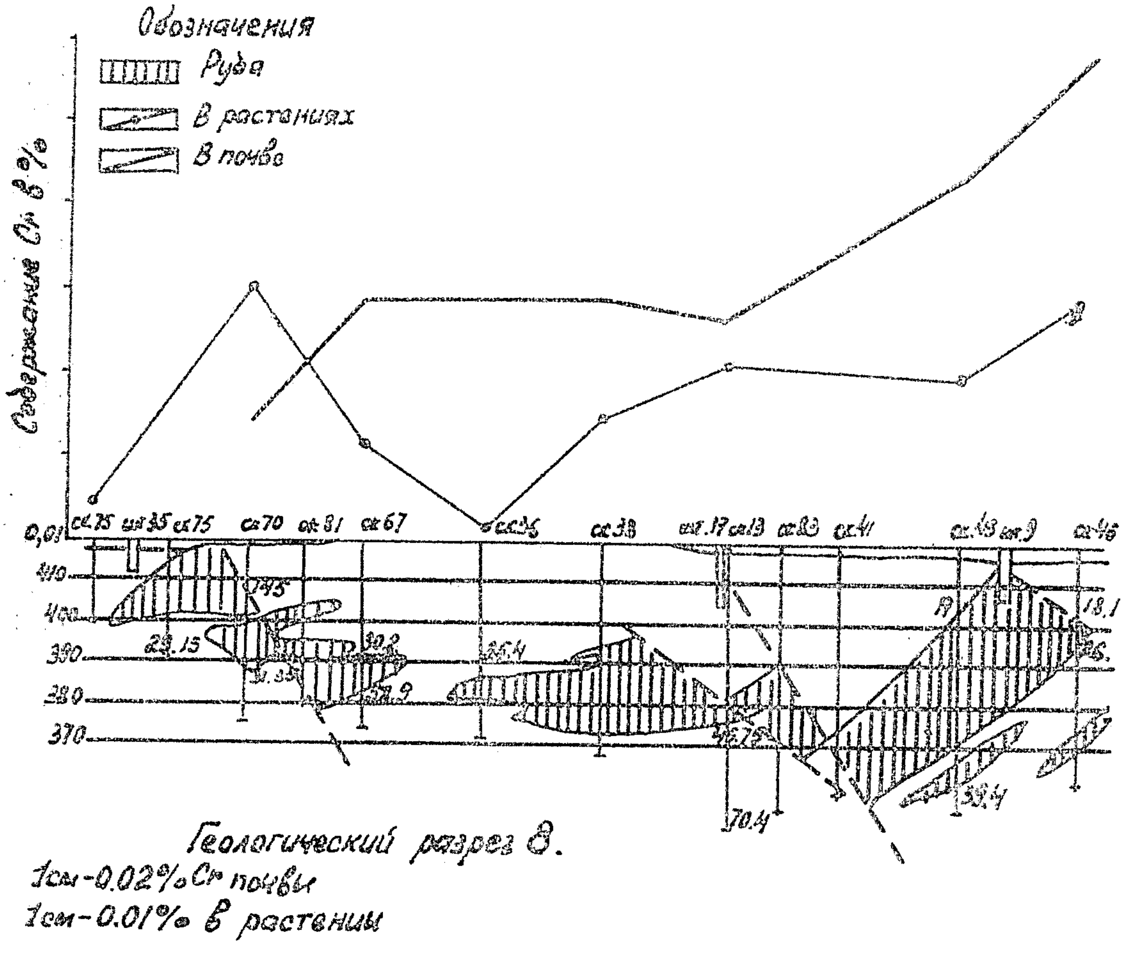

Рис. 12—Распределение Cr в золе растений и почвах в связи с залеганием руды Викторовского месторождения.

ковыльно-типчаковой растительностью. Уровень грунтовых вод, в среднем, находится на глубине 20 м от поверхности, т.е. значительная часть рудной толщи находится в зоне циркуляции подземных вод. Однако в рудничных водах только ок. $1 \cdot 10^{-6}\%$ Cr.

Были систематически изучены растения и почвы на содержание Cr. Вместо многочисленных отдельных определений Cr в почвах мы приводим сводную карточку распределения Cr в почвах этого района (рис. 10).

Нужно отметить содержание довольно значительных количеств Cr в растениях. Практически в почвах и золе растений находились одинаковые количества Cr, чего, как мы видели, не было в случае с Ni (содержание в почвах Ni всегда выше на порядок) (рис. 11).

Между содержанием Cr в растениях, почвах и рудой наблюдалось хорошая корреляция (рис. 12).

3—*Медистые месторождения Бакр-Узек и Южный Юлук в районе Сибая (Урал)*

Месторождения медно-колчеданных руд частично или полностью изменены в карбонаты, которые встречаются в виде включений в сланцах.

Сибай находится севернее никелевых районов, в других географических условиях. Здесь степь очень часто переходит в лес (Ю. Юлук) с оподзоленными почвами.

Почвы под рудой содержали в среднем ок .$10^{-2}\%$ Cu и такое же содержание Cu было и в растениях собранных с этих почв, т.е. подтвердилось то правило о концентрации Cu в растениях и почвах, которое мы наблюдали в отношении Cu и на никелевых месторождениях.

Месторождения Тувинской автономной области

Изученный район расположен в бассейне среднего течения р. Элегеста и приурочен к северной части предгорий у границы Западного и Восточного Танну-Ола.

В геоморфологическом отношении районы можно охарактеризовать как среднегорный, в пределах которого располагается много сопок и гребней, разделенных долинами и оврагами. Район в большей своей части закрыт делювиальными и аллювиальными отложениями и трудно поддается визуальному геологическому изучению.

В геологическом строении района принимают участие древние толщи, характерные для Восточного Танну-Олакембрийские эффузивы и “эффузивно-осадочные” породы верхнего силура и нижнего девона. В пределах района расположено ядро антиклинория, сложено нижнекембрийскими эффузивами с выступающей на поверхность гранитной интрузией, относящейся к нижнекаледонской складчатости. К интрузиям каледонской складчатости приурочено образование ряда сульфидно-арсенидных месторождений Ni, Co, Cu. Морские осадочные породы верхнего силура несогласно залегают на нижнекембрийских эффузивах. В нижней части разреза преобладают песчаники с прослоями алевролитов и карбонатных пород, часто превращенных в скарны; в верхней красноцветные песчаники и конгломераты, на которых образовались почвы.

В сухие периоды времени года район безводен. Подземные воды находятся на значительной глубине и выходы их на поверхность почти полностью отсутствуют. В зоне вечной мерзлоты, на северных склонах сопок, наблюдаются надмерзлотные воды, выходящие иногда на поверхность в виде ключей.

Биогеохимические исследования производились на территории протяженностью свыше 10 км – район р. Он -Кажаа притока р. Элегеста. Наличие линий разломов и других дизъюнктивных процессов на этом участке позволяло предположить наличие здесь рудных обогащений.

Почвы района недостаточно изучены. Они отличаются большим разнообразием – от торфяных горнотундровых до светлокаштановых почв степей. Неоднородность почв вызвана горным рельефом страны. На южных склонах гор вплоть до больших высот располагаются степные почвы, а на северных серые горнолесные и подзолистые почвы.

Растительность на южных склонах злаково-караганниковая, а на северных – лиственичные леса. Большая часть района р. Он-Кажаа, где мы вели работы, покрыта степью со Stipa capillata, Caragana spinosa, C. pygmaea и др.

Очень своеобразна растительность на древних рудных отвалах, выделяющаяся ярко-зелеными пятнами на желто-сером фоне степи. В ее состав постоянно входят Gypsophila patrini, Silene Jeniseensis и др. Эта приуроченность Gipsophilla и др. к медистым рудам была с успехом использована при проведении поисковых работ на р. Он-Кажаа.

Были изучены три участка: а) Южный участок сульфидно-арседнидного месторождения Ni и др. металлов. Жилы секут крутой южный склон горы; б) Северный участок с сульфидно-арсенидным оруденением, причем жилы проходят по борту покрытого лесом северо-восточного склона той же горы: в) участок доль р. Он-Кажаа с медистым оруденением.

Пробы каштановых почв Южного участка по ряду профилей показали значительное содержание Ni, Co, Cu. Содержание Co в почвах колебалось от $1 \cdot 10^{-3}$ до $1 \cdot 10^{-1}\%$, Ni от $4 \cdot 10^{-4}$ до $1{,}9 \cdot 10^{-1}$ и Cu от $1 \cdot 10^{-3}$ до $2 \cdot 10^{-1}$.

Также было повышенным их содержание в степной травянистой растительности – в среднем содержалось Co $7 \cdot 10^{-3}$, Ni $8 \cdot 10^{-3}$ и Cu $4 \cdot 10^{-2}$ и, как видно из рис. 13, нарастало параллельно с содержанием в почвах. Это указывало на сильный ореол рассеяния рудной жилы, не глубоко залегающей от поверхности 1-5 метров. Обращало внимание отношение Ni/Co, близкое к 1.

Совершенно также и в темносерых горнолесных почвах Северного участка оказалось высокое содержание Ni, Co, Cu, содержание Co колебалось от $6 \cdot 10^{-4}$ до $1{,}9 \cdot 10^{-1}$, Ni от $6 \cdot 10^{-4}$ до $2 \cdot 10^{-1}$ и Cu от $1 \cdot 10^{-3}$ до $2{,}5 \cdot 10^{-1}$ %.

В золе листьев и хвои деревьев Северного участка в среднем находилось Co $3{,}8 \cdot 10^{-3}$, Ni $8 \cdot 10^{-3}$ и Cu $4{,}7 \cdot 10^{-2}$. В обоих случаях отношения Ni/Co повторяли отношения для почв и растительности Южного степного участка и также указывали на оруденение (рис. 14).

Наконец, был изучен участок широкой долины р. Он-Кажаа. Профили проб почв нанесены на карточку, где также приведены и оконтурены зоны с разным содержанием в почвах р. Он-Кажаа Ni, Co и Cu. На рис. 15 приводится распределение Cu в почвах р. Он-Кажаа. Данные указали на наличие в пределах обследованного района ряда новых очагов оруденения.

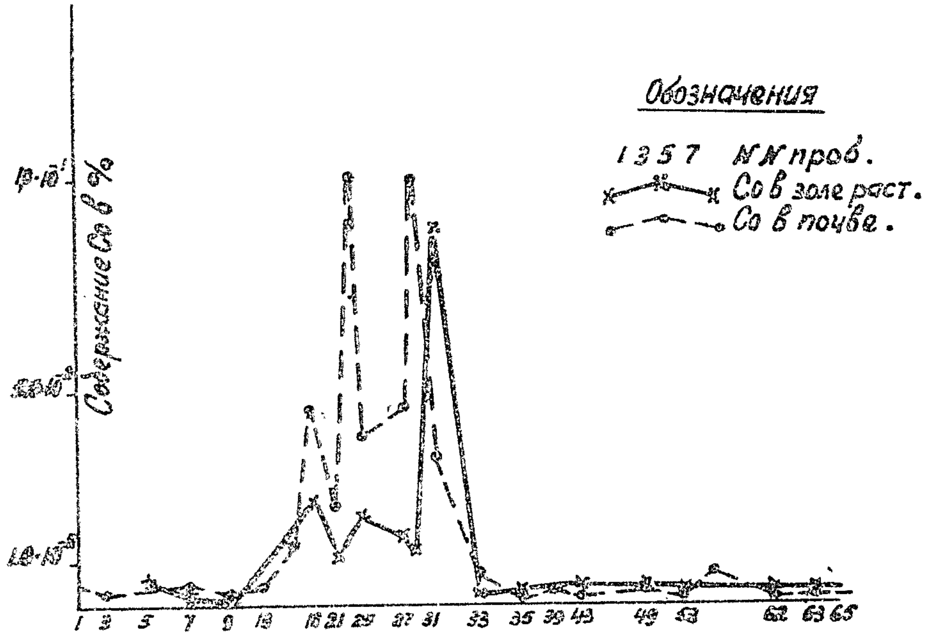

Рис. 13—Содержание Co в почвах и растениях (золе) Южного участка (Тува).

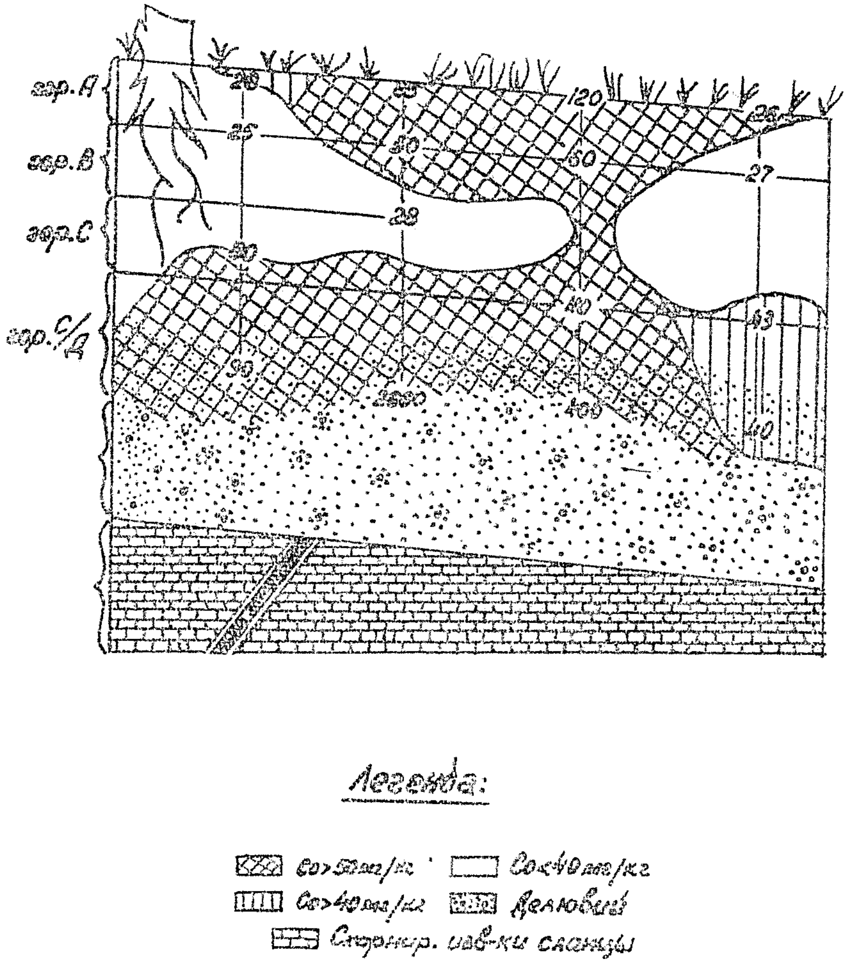

Рис. 14—Ореол рассеяния Co в профиле, над жилой, Северный участок (Тува).

V—ОБСУЖДЕНИЕ РЕЗУЛЬТАТОВ ПРИМЕНЕНИЕ БИОГЕОХИМИЧЕСКОГО МЕТОДА ДЛЯ ПОИСКОВ И РАЗВЕДКИ НА РУДУ

Мы имели возможность применять биогеохимический метод поисков и разведки на руду в очень разнообразных геологических и климатических условиях Среднего и Южного Урала, Восточного Забайкалья, Кавказа, Тувы, причем биогеохимический метод особенно применим в областях обширного развития осадочных пород, моренных осадков или обширного развития песков в пустынях и полупустынях. Образование коры выветривания на плато, в долинах, пологие склоны гор и холмов, покрытые лесом

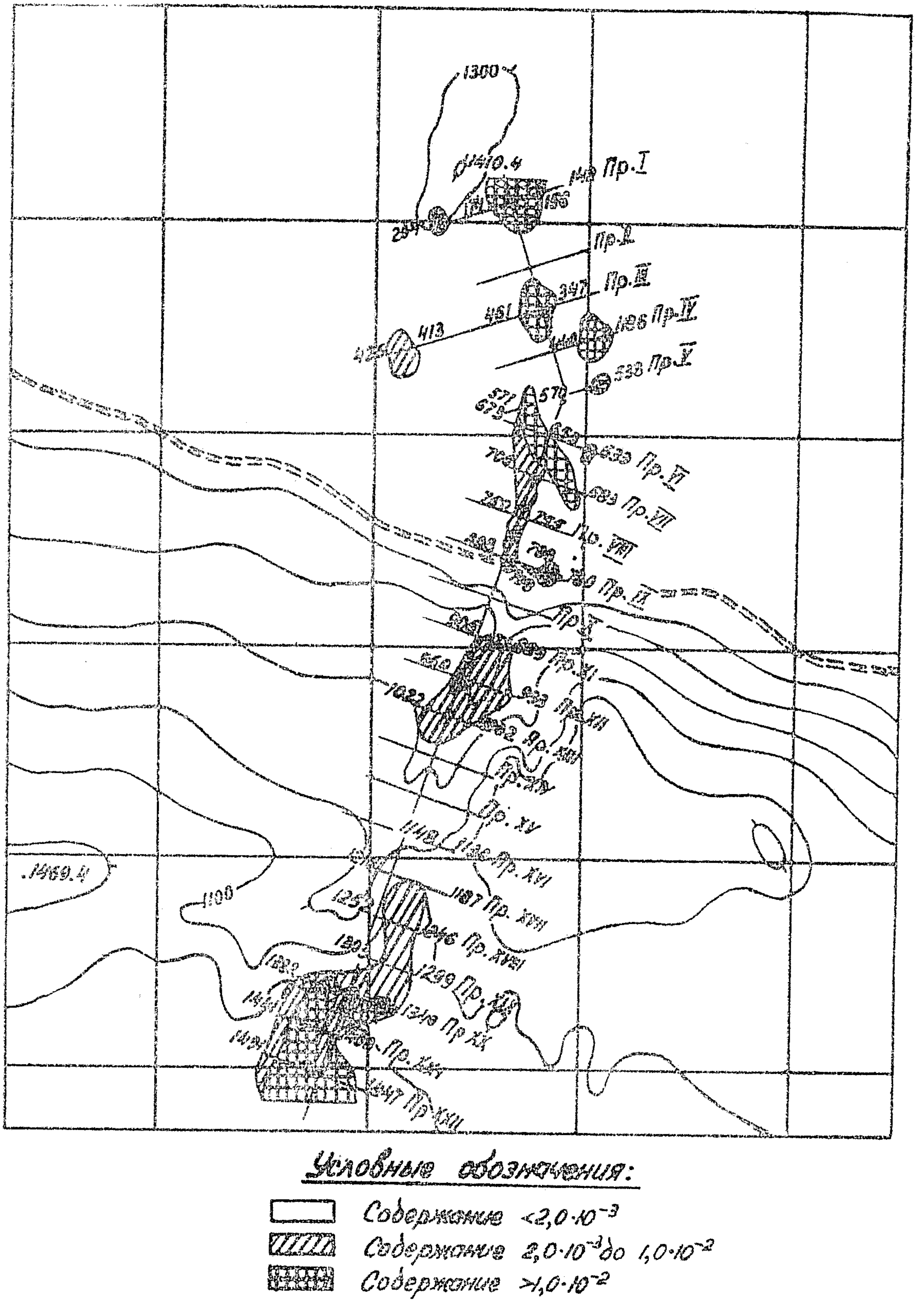

Рис. 15—Распределение Cu в почвах р. Он-Кажаа (Тува).

– это все территории, на которых с успехом можно применять биогеохимический метод. Были поставлены поиски на Ni, Co, Cu, Cr, Pb, Mo. Во всех случаях оказалось параллельное повышение содержания этих металлов как в растениях, так и в почвах, причем увеличение в 10 раз в растениях или в десятки раз в почвах содержания металла против обычного, нормального его содержания, указывало на значительную минерализацию. Наибольшая концентрация металлов наблюдалась в многолетних растениях, с глубокими корнями, с интенсивным водообменом. При всех условиях наиболее выгодно пользоваться при анализе почв – верхним гумусированным горизонтом или пробами из разных почвенных горизонтов, в зависимости от характера почв. Во многих случаях была обнаружена изменчивость морфы ряда характерных растений, произрастающих в районах месторождений. руд.

Исключительное значение представляют отношения, подобные Ni/Co и др., обнаруженные в растениях и почвах.

Серьезное значение при пользовании биогеохимическим методом имеет вопрос, до какой глубины этим методом можно обнаружить минерализацию. Имеющийся у нас опыт показывает, что этим методом в благоприятных случаях можно обнаружить руду на глубине до 50 м. В среднем же эта глубина составляет ок. 10-15 метров.

Этот метод следует рекомендовать в комплексе с другими геологическими методами поисков руды.

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HIDROGEOCHEMICAL METHOD FOR MINERAL DEPOSIT PROSPECTING

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ABSTRACT

Because it has become more and more difficult to find new deposits by the usual geological methods during the last few years, geochemical methods have attracted great attention. Among them great significance must be attached to the hydrogeochemical method based on the ability of chemical elements to dissolve in natural waters and to migrate together with them.

As a result of investigations carried out in the USSR and in other countries it has been proved that the chemical composition of natural waters is to a great extent determined by the composition of the rocks through which these waters circulate, and that the waters passing through deposits of hydrogene elements as a rule are essentially enriched by them. As a result, water halos of dissemination arise with an anomalous high content of elements typical for the deposit, considerably exceeding their natural hydrogeochemical background for the given physical-geographical conditions.

With the aid of thorough investigations it has been proved that for copper, molybdenum, uranium, nickel, and some other elements, a tenfold, hundredfold and sometimes also a thousandfold excess anomaly factor may be easily shown by the existing methods.

The detection of anomalous water halos of dissemination may be carried out in the following way:

a) By sampling the water from suitable natural and artificial water sources;
b) By analyzing them for the desired elements;
c) By interpretation of the obtained data.

Investigations carried out in the USSR have shown that in interpreting the water anomalies it is necessary also to take into consideration the following: the form in which the elements are contained in the rocks and ores; the character of the aqueous solutions; the distance from the place of sampling to the deposit; the climatic conditions; the seasonal and other variations of the water supply; and the geomorphologic pecularities of the drainage areas.

The hydrogeochemical method is one of the most convenient for carrying out investigations at a great depth, and permits under suitable conditions the detection of ore at depths of over 100 m. It is applicable for a large number of hydrogene elements having relatively high clarke concentrations and coefficients of water migration; among these are copper, uranium, molybdenum, lead, potassium, boron, and many other elements.

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ON BIOCHEMICAL PROSPECTING FOR ORES

V. MARMO *

ABSTRACT

The products of disintegration of an ore-bearing rock may be used for ore prospecting. These products can be used, begining with huge erratic boulders and progressing to gravels and soils for prospecting based on the occurrence of the ore minerals themselves. If disintegration is more advanced, the tracing of minerals becomes impossible, and instead, ore prospecting will be based on the cations of economic metals. The latter is geochemical prospecting.

Biogeochemical prospecting is a particular type of geochemical, and it is based on cations which are fixed by the living organisms, particularly by plants. The plants obtain dissolved cations from water in connection with their nutriments. Consequently the type of cations obtained by the plants is governed by the circulation of ground or surface waters; therefore, to interpret biogeochemical investigations the hydrological aspects of an area have to be considered. Different cations have entirely different distribution patterns in water and soils, and this pattern must also be known before the results of a biogeochemical study can be understood.

The physiology of plants is a necessary limiting factor in biogeochemical ore prospecting. Most plants take up copper in their cells to a definite limit, and abviously a similar upper limit exists for some other cations as well. It has been experimentally proved that different parts of the same plant accumulate certain cations in different amounts. Consequently, for each particular cation the most suitable plant must be chosen. This plant must be comparatively common, grow on any substratum occurring within the area to be prospected, and have organs of the same age that can be collected easily.

INTRODUCTION

Unaltered primary ore in Precambrian areas usually forms a continuous body which is enclosed by virtually barren rock. If the body is not sheared or faulted, it is well protected against all types of weathering.

All rocks, however, are fissured and fractured to some extent. Thus the circulating waters are able to affect hidden ore bodies, but the water moves too slowly in minute fissures to bring enough dissolved metals to the surface for geochemical prospecting. Sufficient amouts of cations of heavy metals, therefore,

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* *Geological Survey of Finland.*

may be detected in waters of wells, springs, rivers, soils, or ashes plants only above ore bodies which either outcrop or are concealed by greatly fractured and fissured rocks. If the ore body is entirely covered by solid rock or if it occurs beneath a sufficiently thick layer of sediments, it cannot be detected by either geochemical or biogeochemical methods. This fact is an important limitation as the advance of mining has made it necessary to find deep-seated ores.

Only ore bodies that outcrop from embracing barren rock can be detected by geochemical or biogeochemical methods. In other words, there must be places where the ore body occurs without any solid rock cover. It may be covered by loose sediments or its rock cover must be comparatively thin and extensively fractured; the ore will then be subjected to the processes of disintegration.

During the disintegration of the rock, first big boulders and blocks will result which may be displaced or lie *in situ.* Upon more extensive disintegration gravels result —the smaller particles going into clays, sands, and soils— and with time part of the ore will be dissolved by water and go into solution.

From the point of view of the ore prospector, the ore minerals are of primary interest. They may be detected in the products of disintegration if they are not too finely dispersed. If the material is too finely dispersed, the heavy metals of the ore may still be traced in the form of cations. These can be detected by chemical analysis of soils, waters, and of plants which obtain their nutriment from the circulating waters. Therefore, all products of disintegrated ores can and have been used in ore prospecting.

In general, the coarse products of disintegration which contain preserved ore minerals are not considered to belong in the geochemical field. Geochemical methods are concerned with the finer products, and they are based on the tracing of cations, not of minerals. The biogeochemical method is based on living organisms or remnants of them. It traces the cations accumulated by them, mainly using plants.

All these methods, however, are closely linked to each other, and roughly, boulders, gravels, soils, waters, and plants form a series corresponding to the increasing halos of dispersion.

TRACING OF BOULDERS, GRAVEL, SAND, AND SOILS

In most parts of the world big boulders or rocks occurring on or at the surface of the earth are of more or less local origin. Hence, if a boulder rich in ore is found, its parent rock may be found not far from the site of the boulder itself.

In countries which have been glaciated the problems are not as simple as in countries which have not been glaciated. In glaciated areas the boulders have been transported during glaciation far from their parent rock and may be found several kilometers from their place of origin. In countries which have not been glaciated, however, transported boulders may also occur. There the transporting agents are gravity and streams. In both of these areas the type of transport and the direction have to be carefully considered. This method of ore prospecting is very well known, and vast amounts of ore have been found in the above manner.

If the disintegration of ores is more complete, then the boulders will be destroyed and gravels, sands, soils, and clays are produced. Under these conditions only a few ore minerals survive, and most of the sulfides are disintegrated by weathering because the cations of the sulfides go into solution easily.

These products of disintegration in most parts of the world are transported only by gravity or running water. In the countries which have been glaciated the gravels, sands, clays, and soils may be transported far away from the place of their derivation, and therefore, the glacial geology of these areas must be considered when prospecting for ore. If these disintegration products are generally local as they are in tropical countries, the concentration of heavy metals in the soils may directly indicate the outcrop of the ore body beneath the soils.

For ore minerals that are stable, ordinary panning is the most convenient method of prospecting. It has been used very successfully for diamonds, gold, platinum, cassiterite, columbite, tantalite, ilmenorutile, chromite, etc.

The chemical analysis of soils is based on the assumption that the soils contain the cations of the disintegrated ore more abundantly on or near the parent ore. Here we enter the fields of geochemical prospecting. This type of prospecting, which is very well discussed in the literature, is not, however, entirely dependent upon the remnants of ore minerals, but to a large extent it also depends upon the cations brought into the soils from the surrounding area by circulating water. Thus the types of cations being dissolved by the water are of utmost importance for interpretation of the results. I should say that this factor is of more importance than the presence of mineral remnants in causing geochemical soil anomalies.

METAL CONTENT OF WATER

The dissolved heavy metal cations of ores are distributed further from the original source in water than in soils. Thus by tracing the cations distributed in the drainage systems, indications of ore may be detected over a larger area than when using the other disintegration products discussed above. There are many rapid and good analytical methods for the determination of small amounts of cations in soils and waters, which make this prospecting method comparativly easy to use. A close relationship between the ore bodies and the cation content of circulating waters has been found in most areas. On the other hand, from a study of well waters of a limited and geologically well studied area at Nokia, Finland (Marmo, 1953), it was found that small quantities of copper and zinc in the rock are clearly reflected by the content of the corresponding cations in well waters.

When water is used in prospecting, the direction of the flow must be exactly determined. The direction of flow in small streams is, therefore, usually insufficient for this purpose, and it must be determined from the topography what are the sources of the river waters. Consequently, a complete picture of the general hydrology of the area investigated must be well known. If a hilly country is to be investigated the topography is considered to be of great importance in interpreting the results of geochemical investigations. The determination of the flow of the water in flat areas may sometimes involve a great deal of difficulty.

BIOGEOCHEMICAL METHOD

Because there are several vast areas which are interesting from the geological point of view for ore deposits but which contain very few streams, other means of investigating the underground waters of these regions had to be found. The plants growing in such areas may control variations in the heavy metal content of sub-surface water. In many areas the study of plant ash may be the best method to be used because plants actually concentrate the heavy metals in their tissues, obtaining these metals from the circulating waters, the source of their nutriment. Hence the cation content of the water and also of the bedrock or soils. The biogeochemical method is concerned with plant ash.

In this connection the so-called geobotanical method will not be discussed. It may only be mentioned that geobotanical ore prospecting is much older than biogeochemical. Geobotanical prospecting is based on the fact that some plants will prefer soils which contain certain minor elements in unusual quantities. The lime plants are well known. Some plants, such as *Viola calaminaria* prefer soils rich in zinc. Some species indicate copper, and in Sierra Leone it was observed that if in a granitic area sword grass occurred in exceptional abundance, then invariably serpentinite or amphibolite was also found.

The biochemical method requires that acertain plant be common over the entire area to be investigated. In comparing the analyses of some common plant or herb ashes, the higher contents, for example, of copper, may indicate a biogeochemical anomaly which in turn may possibly indicate copper ore or at least an unusually high copper concentration in the bedrock.

Most of the authors who have worked in the field of biogeochemical prospecting report successful results. They have usually investigated known the metal content in the ash of plants growing over these ores. So also did the writer in regard to copper, lead, zinc, and nickel in the rock of Finland (Marmo, 1953), but he also Pointed out that there is so far no conclusive evidence which would directly incate the value of the deposits found by this method. Furthermore, the botanists have found that many plants concentrate certain metals, for example copper, only to a definite limit. Until these limiting concentration values for the plants which are to be used in an area are konwn, the method is still insufficiently interpretable. The are still little data pertaining to biogeochemical prospecting for unknown ores.

There is probaly little doubt that the biogeochemical method is useful and in the future will increase in value. Before this can happen, however there must be more preliminary investigation in close collaboration with botanists experienced in the physiology of plants.

PROBLEMS CONCERNING THE BIOCHEMICAL METHOD

Plants obtain both their nutriment and their heavy metals from the circulating ground waters. Some of the economically significant metals are necessary to maintain plant life; others may be poisonous if obtained in large amounts. For example, an excess of vanadium, manganese, and molybdenum may cause diseases in the plants and prevent their growing. As was mentioned above, some plants accumulate certain elements to a definite limit, but not in excess of that limit. In some herbs this limit may be below that necessary for indicating economic ores, and the maximum content of certain metals, for example copper, may be obtained from ground waters leaching rocks which contain sparsely disseminated chalcopyrite and then appear on the graphs as a definite anomaly.

All the physiological aspects of the plants must be considered in choosing a herb for prospecting for some particular ore. I have found for *Ledum palustre* in Finland (Marmo, 1955) that this plant concentrates copper more in its twigs than in its leaves; this type of distribution has not been observed for molybdenum in this plant.

The second and much more important problem is deciding upon the type of plant to sample in the area. There are two types of water circulating underneath the surface and supplying the plant with nutriment. They are ground water and vadose water. Both of them are able to leach ores or ore minerals from the soils or dissolve the salts deposited secondarily in the interstices of the soil grains. Ground water has a much greater circulation than vadose water has a much greater circulation than vadose water. Depending upon the capillarity of the soils, ground water may or may not reach the surface, but there are plants which normally do not reach ground water with their roots; others, on the contrary (trees, shrubs, and some herbs as for example *Vaccinium vitis idaea*) reach ground water if the water table is not at too great a depth; therefore, different plants with different root systems will yield different records for the biogeochemical prospector within the same area.

From the previous discussion of the different stages of disintegration of an ore body it can be seen that there are different patterns of distribution of different disintegration products. These patterns affect all the geochemical methods, but they affect the biogeochmical method even more than the others. In areas which have been glaciated, the direction of glacial transport affects

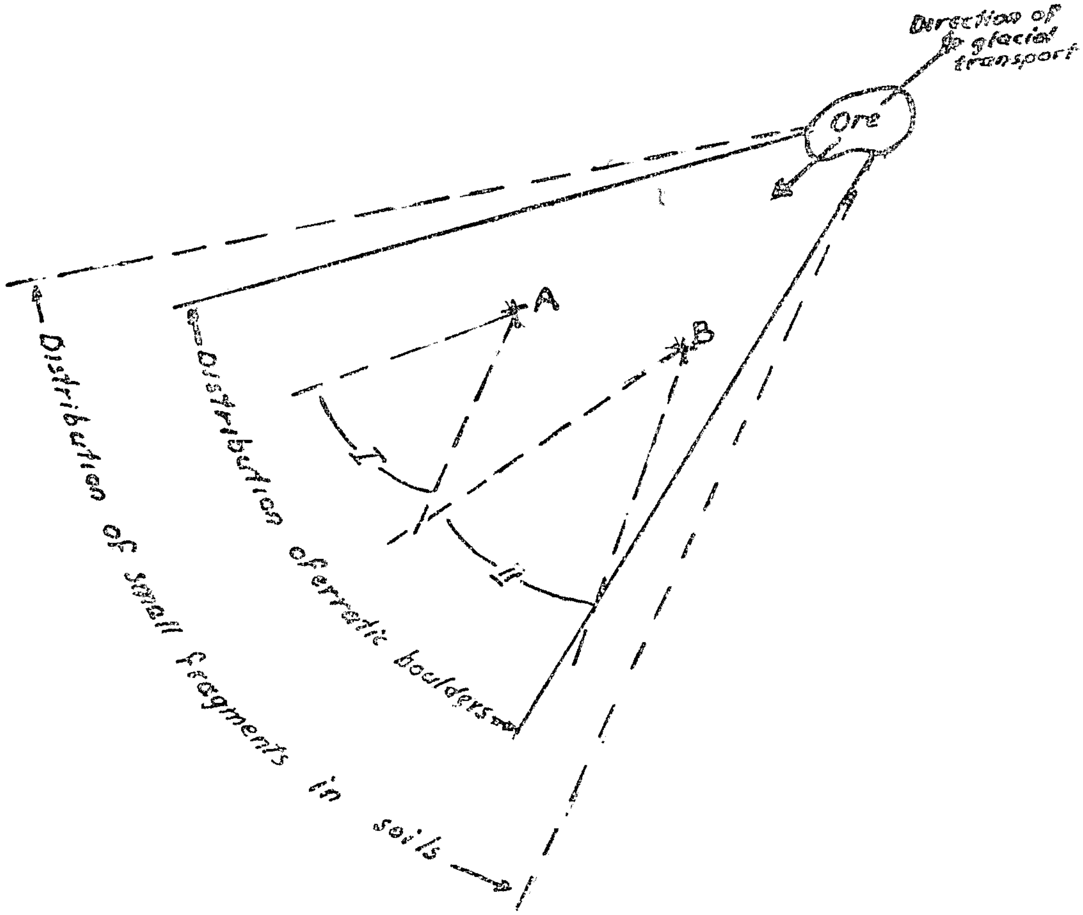

Fig. 1 Distribution of ore fragments due to glacial transportation. A and B are large erratic boulders which due to more advanced disintegration produced new secondary fans L and LL.

all the stages of the disintegration of the ore because the coarsest products like boulders and blocks still continue desintegrating and produce new halos of distribuition. This situation is illustrated in Fig. 1. The circulating waters obtain their cations from the area surrounding an outcropping ore body, and if the direction of flow of the ground water is the same as that of the ancient glacier movement, the anomalous area will extend in the same direction but remain a narrow train. If the ground water flows in the opposite direction to the glacial movement, indications of the ore will be found on both sides of the ore body (Fig. 2A). If the flow and ice movements make an angle, the distribution pattern may be rather complicated (Fig. 2B) and may fail to indicate even large ore bodies.

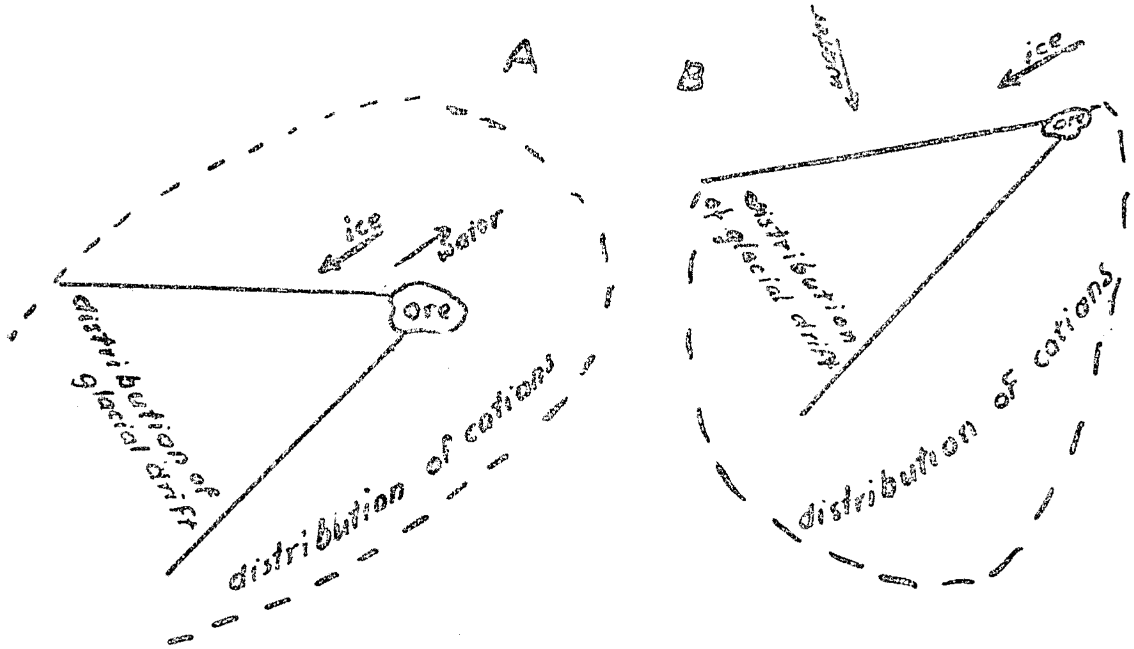

Fig. 2 Distribution of actions due to glacial transport in a moraine and the subsequent action of ground (or superficial) water. A: The directions are opposite; B: The direction of water flow is subvertical to the direction of the ancient movement of ice.

In non-glaciated areas the distribution pattern is simpler; there it depends on the topography. At Nokia in Finland I definitely found a shift of anomalies in the direction of the flow of the ground water, and this shifting was greater for plants than for well waters

The situation is much more complicated if the soil cover is thick, because the heavy-metal-bearing soil may then give rise to new biogeochemical anomalies; this time in the direction of the flow of surface waters (Fig. 3). If plants are used, the biogeochemical anomalies will apparently extend over a much larger area than the corresponding geochemical anomalies obtained from the soils or streams.

SAMPLING

The biogeochemical method has an advantage over the geochemical soil method in that it is based on a larger halo of distribution, and over the stream-water geochemical method in allowing the sampling to be done on a network or grid pattern.

Sampling along widely spaced lines, as mostly used by geochemical prospectors, has severe disadvantages because it leaves open the areas on both sides of the lines and does not show the form of the geochemical anomaly which is helpful in showing the pattern of distribution. If the biogeochemical method is used, a much more elaborate sampling procedure is necessary. One must set up grid of samples covering the entire area in question. The density of the network of samples depends upon the accuracy desired. If the metals to be used in prospecting are not easily soluble and the size of their economic ore bodies are small, the density of samples must be greater than if metals are used which are easily soluble and the size of their economic ore bodies are large (for example, copper and zinc). For soils a more dense sampling grid is required than for water or plants.

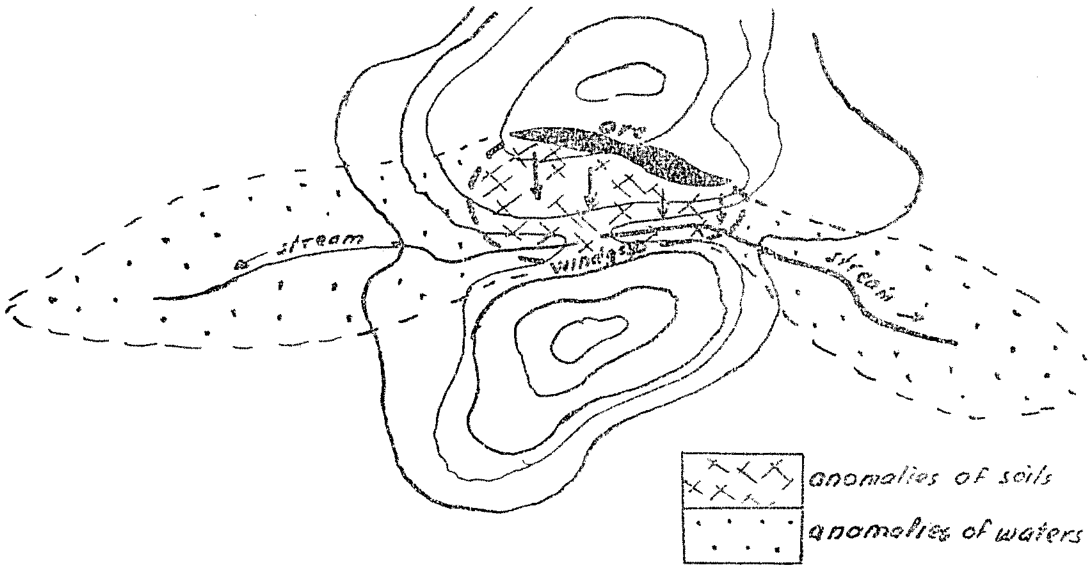

Fig. 3 Distribution of cations, derived from an ore, in soils and in water due to topographical features. The ore is on the slop above a windgap. In soils the anomalies are mainly found between the ore body and the windgap, but in water they extend in the direction of streams on both sides of the windgap.

A convenient sampling pattern can be made by placing several parallel lines across the strike of th estrata. If the dip of the rocks is very flat and the ores tend to be concordant with the strata, the direction of the lines is of less importance. The distance between the adjacent lines should not be more than the minimum length of economic ore body for the metal being sought. If we were prospecting for nickel, cooper, or zinc, we found the appropriate distance between each line to be about 100 meters. The interval of sampling along each line is determined by the minimum breadth of an economic ore body. Furthermore, the sampling interval depends upon the topography of the area to be prospected. On slopes dipping in the direction of the lines the interval may be longer than on flat areas. The author has used intervals of 50 to 80 meters, and in his opinion the results obtained have been rather satisfactory.

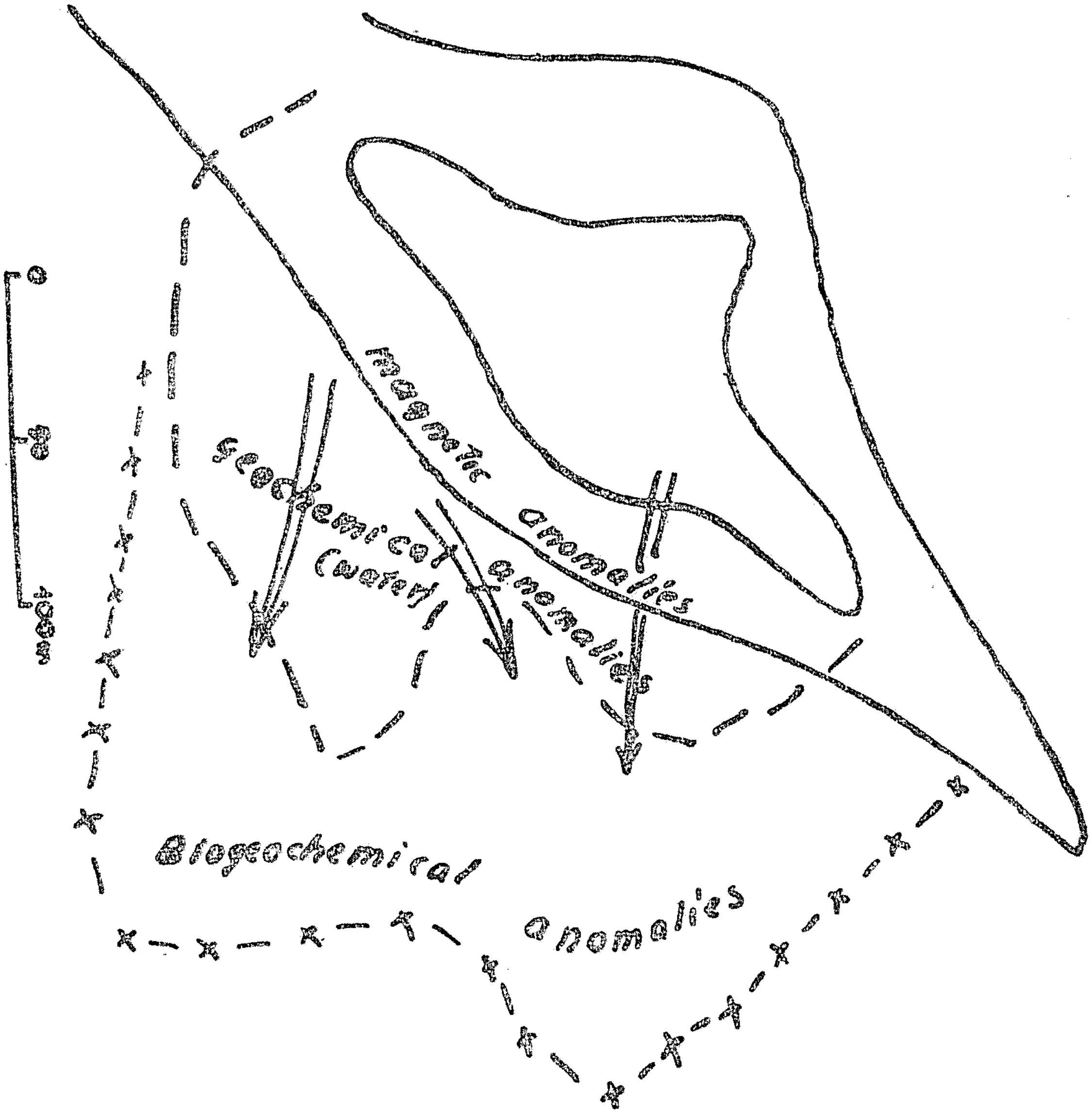

Fig. 4 Relationship between magnetic, geochemical and biogeochemical anomalies in a portion of the Nokia Region, Finland. The arrows indicate the flow of ground waters.

The chemical treatment of plant samples involves considerable expense because the samples have to be ashed. The size of a biogeochemical sample depends upon the plant used. In general the plants contain 3 to 8 percent ash, that means from 100 grams of air dried plant, 3 to 8 grams of ash can be obtained. Rarely the ash may contain 2 to 3 percent zinc; the ash usually contains about 50 ppm of zinc or less than 20 ppm copper. Both values would indicate an anomaly. In 10 grams of ash of leaves or twings there may be less than 0.5 mg Zn or less than 0.1 mg Cu. The sensitivity of the chemical method to be used also determines the size of the sample. If spectrochemical methods are used, about 30 grams of air dried sample is sufficient.

The selection of suitable plants is of importance. The same plant must be common throughout the area to be investigated. If the area in question is large, it is often difficult to find such a plant. Then two plants may be used, each typical of a separate part of the district, for example savannah, secondary-bush country, and marsh. At some place in the area both plants should be collected from the same sampling points and thus obtain a comparison of the results of sampling the two different plants.

INTERPRETATION OF GEOCHEMICAL AND BIOGEOCHEMICAL DATA

If all the sampling points are indicated on a map and the points of equa-metal values are connected, a system of curves is obtained. Such a map is the best way of clearly showing the distribution of desired elements and usually gives at once an idea of the possible concentrations of metals within the area. In fig. 4 such curves have been drawn for the distribution of copper in both well water and plants of the same area. Fig. 4 also showns the magnetic anomalies caused by the dissemination of pyrrhotite and chalcopyrite in the schists. The magnetic curves also show a more or less accurate distribution of the sulfides. Both geo- and biogeochemical anomalies are distinctly displaced in the direction of the ground water flow in this area.

If biogeochemical anomalies are obtained in geologically unknown areas, ore concentrations would not normally be expected under the maximum anomalies. The ground water flow must be taken into account in a unknown area. Thus before biogeochemical anomalies can be interpreted, a study of the topography and hydrology of the area is necessary. This also applies to geochemical anomalies found in such an area.

An important question is what is the magnitude of an anomaly which indicates ore? This question cannot be answered: It is not possible to answer this question for geochemical prospecting because the answer depends on many factors: the thickness of the soil cover, the sorting of soils, the presence of boulders in the soils, the presence or absence of gossans, the velocity and amount of circulating water, and the amount of metals being carried by the water. In biogeochemical prospecting the physiological characteristics, as mentioned above, of the plants must also be considered.

USE OF THE BIOGEOCHEMICAL METHOD

Biogeochemical prospecting is rather expensive and slow. In this respect it cannot be compared with geochemical methods which are now comparatively rapid, but still quite expensive.

In my opinion neither geo– nor biogeochemical methods can compete which the modern and rapid geophysical methods, but they both may be, and in certain cases they virtually are, of great importance as a supplementary means of ore prospecting. Some examples may explain this statement.

In Scandinavia pyrrhotite and graphite in the form of thin but rich disseminations in schists is rather common. Both magnetic and electrical geophysical methods are used there widely and successfully. The aforementioned minerals always appear as the source of strong geophysical anomalies. As a means of testing whether the strong anomalies caused by pyrrhotite and graphite also indicate a concentration of economically important sulfides, the present author proposed that geo- and biogeochemical methods be used. I think that for such purposes these methods are very useful indeed, and they have already been used there to determin the pattern for diamond drilling.

Even in economically important ores some metals occur in such small amounts that they cannot be detected by geophysical methods. If the minerals of these metals, in addition, are very unstable during weathering (for example, molybdenum), the geo- and biogeochemical methods are obviously very useful.

These methods may also be very useful in studying areas covered by drift or laterite, which are very interesting geologically but for some reason cannot be studied geophysically. Examples of such areas may be seen in plateaus covered by thick clay leyers or by thick laterites rich in hematite, which cause strong geophysical anomalies.

Geo- and biogeochemical methods may be very useful in prospecting laterite-covered areas of the tropics, but before these areas can be prospected, studies of laterites will have to be carried out. I do not believe that good results can be obtained except by accident if men are sent to the tropics to collect and analyse samples without first carefully studying the topography, hydrology, and geologic conditions of the areas. In my opinion geo- and biogeochemical prospecting are not matters of good chemists and then blind collecting of samples, but a matter of field research in close collaboration with able analysts.

The suitability of a laterite for geo- and biogeochemical prospecting is interesting, but it is not a simple question. Dealing with soils, we are working with cations of the circulating waters and with those metals retained or precipitated by the soils. However, in prospecting a laterite it is of less importance to find residual laterittes. The transported laterites, or lateritized gravels and soils which metals are being leached from the laterites. This particularly applies to the residual laterittes. The transported laterites, or lateritized gravels an dsoils which are not uncommon in the tropics, involve entirely different problems that may be of such a character they make these laterites useless for prospecting by the methods considered above.

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