Geochemical Cycle of Selected Trace Elements In the Tin-Tungsten-Beryllium District Western Seward Peninsula, Alaska A Reconnaissance Study

By C. L. SAINSBURY, JOHN C. HAMILTON, *and* CLAUDE HUFFMAN, JR.

CONTRIBUTIONS TO ECONOMIC GEOLOGY

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A study of the geochemical movement of certain trace elements from sedimentary and igneous rocks into contact rocks, minerals, and ore deposits, thence into soils, stream sediments, and plants

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GEOCHEMICAL CYCLE OF SELECTED TRACE ELEMENTS IN THE TIN-TUNGSTEN-BERYLLIUM DISTRICT WESTERN SEWARD PENINSULA, ALASKA-**A RECONNAISSANCE STUDY**

By C. L. SAINSBURY, JOHN C. HAMILTON, and CLAUDE HUFFMAN, JR.

ABSTRACT

A reconnaissance study of the geochemical cycle of tin, beryllium, boron, lithium, tungsten, copper, lead, zinc, and niobium in the tin-beryllium district of the western Seward Peninsula, Alaska, shows that the biotite granite stocks are enriched in beryllium as compared with other tin-granites, and that most elements moved outward from the stocks into the thermally metamorphosed rocks aiid skarns around the stocks. Following the consolidation of the exposed granites, a strong set of normal faults developed in the central York Mountains; dikes of rhyolite, rhyolite porphyry, diabase, arid lamprophyre were injected into many of the faults. After the faulting and the injection of dikes, lodes of tin, tungsten, beryllium, and fluorite were formed in which all the trace elements were greatly enriched. Individual minerals from the lodes contain anomalous amounts of trace elements and, irrespective of their position in the zoned ore deposits, point clearly to the passage of solutions enriched in the elements studied.

In supergene processes, clearcut geochemical anomalies were formed in stream sediments, soils, and plants of the area. Except possibly for zinc and silver all the elements investigated remain associated throughout the geochemical cycle. Tundra plants concentrated most elements to a degree, but for beryllium, and to a lesser degree tin and niobium, there is a point at which soil concentration invariably exceeds that of plant ash. The single lichen investigated concentrates silver but has a low content of other elements.

Anomalous amounts of many rare metals in igneous rocks can possibly host be detected by analyses of the bulk heavy-mineral fraction having a specific gravity greater than that of methylene iodide (3.29).

INTRODUCTION

In the western Seward Peninsula, Alaska *(fig.* 1), several stocks of biotite granite intrude slate and limestone. Tin and tungsten deposits near the granites have been known since 1902 (Collier, 1902) and were

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FIGURE 1.-Location of study area.

described in some detail by Knopf (1908). Between 1960 and 1964, significant deposits of fluorite containing beryllium minerals were discovered as a result of geologic mapping by the U.S. Geological Survey (Sainsbury, 1963). These discoveries extended the knowledge of the geochemical association of tin and beryllium that has become apparent in the few years since Eankama and Sahama (1950, p. 446) stated that minerals and rocks associated with pneumatolytic deposits of cassiterite were not enriched in beryllium. Several authors of more recent literature have discussed the association of beryllium with tin (Warner and others, 1959, p. 40; Beus, 1962, p. 39; Lesure and others, 1963), and have noted the role of fluorine in regulating the association of tin and beryllium (Beus, 1962, p. 38; Warner and others, 1959, p. 40). On the basis of the similarity between the beryllium-bearing fluorite replacement veins of the Sewaxd Peninsula and those Kussian deposits discussed by Beus (1962, p. 87-96) and Govorov (1958), Sainsbury (1964a) pointed out other areas in the world where beryllium deposits should be sought in or near tin deposits characterized by lime-

GEOCHEMICAL CYCLE OF TRACE ELEMENTS **F3**

stone wallrocks and a high fluorite content.¹ Today the geochemical association of tin, tungsten, beryllium, and fluorine in greisen-type tin deposits is probably an accepted fact, and the general association of fluorine and beryllium is probably more widespread than was once thought. For example, significant deposits of beryllium have been found in the Western United States in the areas where the fluorine content of silicic volcanic rocks is relatively high (Coats and others, 1963).

Although the main geochemical associations outlined above are well known, less information is available on the association of some elements, such as lithium and boron, with tin, beryllium, and fluorine in igneous rocks and in ore deposits. Furthermore, virtually no information is available on the geochemical fractionation of these elements among the rocks and minerals of a tin-tungsten-beryllium province, such as that of the western Seward Peninsula and of other areas where new associations are being found. For example, although the beryllium deposits in Utah have been known for several years (Staatz and Oriffitts, 1961), only recently were these deposits found to contain large amounts of lithium and anomalous amounts of tin (Shawe and others, 1964).

This study presents data on those elements that are commonly associated in the tin deposits (tin, tungsten, beryllium, lithium, copper, lead, and zinc) or that are especially common in granites (such as niobium). The work discussed herein is but a small part of a much larger study of the structure, stratigraphy, and ore deposits of the central York Mountains, and the reader is referred to other reports for detailed information to augment the data presented here (Sainsbury, 1965a, b). The authors do not claim this to be a complete study, and two specific areas of weakness should be noted: (1) the number of analyses of sedimentary and metamorphic rock (table 2) is too small to establish the variations within these thick units; and (2) the minerals analyzed from the beryllium ores (table 6) were separated from very fine grained material, and four of them, which contained some impurity that could not be separated, may include a minute amount of discrete beryllium mineral.

The data and scheme of presentation trace the specific elements from bedrock types through the contact rocks and ore deposits and thence through the supergene cycle.

Acknowledgments. The fieldwork for this study was done in 1960-64 by Sainsbury, aided by Donald Grybeck, Thomas E. Smith, D. W. Peters, and J. M. Kelly, geologic field assistants. Analysts other than the authors who participated in this study are named in the tables

¹ Dr. Noboru Hida, Geological Survey of Japan, stated (written commun., 1966) that beryllium now has been found m fluorite veins in the tin districts in Japan discussed by Sainsbury (1964a).

where the particular data are reported. Discussions with W. R. Griffitts, D. R. Shawe, L. B. Riley, and D. E. Lee proved invaluable. The tundra plants were identified by H. T. Shacklette, botanist, U.S. Geological Survey, and some were separated and cleaned by W. H. Raymond. All mineral separations were made by Sainsbury. The assistance of all persons taking part in this study is gratefully acknowledged.

GENERAL GEOLOGY

In the western Seward Peninsula, the main rock units are slate, graywacke, and argillaceous limestone of pre-Ordovician age, and a thick sequence of limestone, dolomitic limestone, and argillaceous limestone of early Paleozoic age, principally Early Ordovician. Coarsegrained biotite granite stocks intruded the rocks in Late Cretaceous time, piercing extensive thrust sheets in the central York Mountains. Numerous dikes of rhyolite, rhyolite porphyry, granite, and lamprophyre were intruded into fractures of a regional fault system whose faults trend N. 60°-85° E. Near the granite stocks, calc-silicate rock and biotite-andalusite hornfels have formed from limestones and slates, and, locally, extensive masses of vesuvianite (idocrase) were formed near granite.

After injection of the dikes, tin and beryllium deposits were formed generally near or in dikes near biotite granite; the tin deposits are generally nearer the granite. The tin deposits consist of cassiterite, minor amounts of stannite, and numerous other sulfide minerals in quartz-topaz greisen and are similar to many other tin lodes of the world. The beryllium lodes are replacement veins, veinlets, and stockworks in limestone and consist of a fine-grained mixture of fluorite, diaspore, white mica, and chrysoberyl and minor amounts of euclase, bertrandite, phenakite (?), todorokite, and hematite. A marked zonation is shown from cassiterite-sulfide deposits to beryllium deposits; transitional veins contain stannite, galena, arsenopyrite, and ferran sphalerite in addition to fluorite, chrysoberyl, and white mica. For a fuller description of the tin deposits see Knopf (1908), and for recent information on the beryllium deposits and regional geology of the western Seward Peninsula see Sainsbury (1963,1965b).

METHODS

SAMPLE SELECTION

The samples analyzed were selected by several methods. Samples of sedimentary and metamorphic rocks were selected randomly from a large suite of hand specimens gathered during field mapping. Most were fist-sized pieces broken from outcrops and give an idea of only the general trace-element content of rock types. Samples were insuffi-

cient in number to establish a concentration of the trace elements listed in table 3 and 4 for the entire rock units involved.

In sampling the granite stocks, most of which are less than 1 square mile in outcrop area, about 100 pounds of granite was obtained at random locations by breaking individual boulders of granite and selecting a pound or more from each. Fresh granite from Brooks Mountain and Tin Creek was obtained by breaking unweathered boulders in the creek beds; these boulders presumably were more representative than surface samples alone would have been. Granite from the Lost River mine was obtained from the mine dump for material taken from drifts that penetrated the granite. The samples from each location were crushed to $\frac{1}{2}$ -inch size, and a split of about 10 pounds was crushed to pass through a 40-mesh screen. The tramp iron was then removed with a hand magnet (the granites contain no magnetite), and the remainder of the crushed material was then powdered for analysis. Although minor lithologic variants are combined in the sample, each analysis probably represents closely the trace-element content of the stock.

The samples of dike rocks analyzed were fist-sized specimens from small dikes and a composite of several specimens from larger dikes.

Minerals submitted for analyses were prepared by gravity methods using heavy liquids, centrifuge, and magnetic separation. A representative sample was ground in a porcelain mortar to pass through a 200-mesh screen and sized in cloth screens. It was then centrifuged repeatedly in heavy liquid whose gravity was adjusted so that a representative piece of the mineral alternately floated and sank. The final product was scanned through a microscope, and a small amount was ground in distilled water and made into a smear on a glass slide, which was X-rayed to check the purity of the sample and the identification of the mineral. The glass smears and the X-ray diffractometer tracings were retained for future inspection. The degree of purity of the samples analyzed is given in the tables. Contamination by heavy liquid was tested for by comparing spectrographic analyses of two fractions of the same mineral, one of which had not been treated in heavy liquids. The results showed no contamination by heavy liquid.

Stream sediments were obtained from material in the lee of boulders, where possible, and most material passed through a 40-mesh screen. In a few places, larger volumes were screened through steel screens to obtain a sufficient sample. The analyses represent the total unsorted sediment.

Soil samples were selected in Lost River valley along two traverses which cross a mineralized fault zone. Control samples were taken

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from unmineralized areas approximately 1 mile north of that area. All the soil samples came from a zone of yellowish clay soil about 1-2 . inches thick which is thinly veneered by pebbles and which grades downward into admixed clay and frost-broken limestone bedrock.

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A clump of tundra also was sampled near each soil-sample locality. In some tundra clumps, individual plants were separated and submitted for analysis. Plants were washed and massaged repeatedly in distilled water, dried, and ashed by heating gradually to 500° C in porcelain crucibles. Owing to the intimate association of soil and plant material in some plants, it was impossible to completely free the samples from soil. The trace-element content of the plant ash is reported as the relative change in concentration in plant ash with respect to the soil in which the plants grew. If the content of an element in plant ash exceeds that of the soil in which the plant grew, the plant, in terms of solids, has concentrated that element. The difference is reported as a plus value in table 12; if the ash contains less of an element than the soil, the difference is reported as a minus. The exact amount assignable to the plant cannot be computed because of the contamination problem.

ANALYSES

The analytical results of this study are taken chiefly from semiquantitative and quantitative spectrographic work by Hamilton. Other analytical work was done by different analysts in three of the U.S. Geological Survey laboratories. Special studies of the precision of analytical results by different Survey laboratories have been made (Rader and Grimaldi, 1961; Barnett, 1961a). Such studies were planned specifically to provide reliable information on the confidence limits of Survey analytical data, not only on the agreement to expect between laboratories but also on the agreement between analysts in the same laboratory. A program of cross-checking is continuously used in the laboratories to improve the precision as well as the methods used. Thus, data from the different laboratories should be equivalent.

The sensitivities and detection limits of the six-step semiquantitative spectrographic analyses are summarized in table 1. This reporting system is more recent than others previously used (Barnett, 1961a), but the general method and technique are the same as described for semiquantitative analyses by Myers, Havens, and Dunton (1961). The quantitative spectrographic method and its reliability were described by Bastron, Barnett, and Murata (1960).

The chemical composition of the granites was determined by the rapid rock analytical methods described by Shapiro and Brannock (1962). The fluorine content of the ore samples (table 6) was determined by the method of Rader and Goss as described in Coats, TABLE 1.-Sensitivities and detection limits of six-step spectrographic analyses

[Semiquantitative spectrographic analyses are reported in percent to the nearest number in the slx-step series 1.0, 0.7, 0.5, 0.3, 0.2, 0.15, and 0.1, etc., which represent approximate midpoints of group data on a geometr percent of the time]

Goss, and Rader (1963). Beryllium was determined by a modification (Patten and Ward, 1962) of the morin-fluorescence method, and the fluorescence was measured with the instrument described by Parshall and Rader (1957). Tin was determined with dithiol as described by Huffman and Bartel (1965), and tungsten was determined as described by Rader and Grimaldi (1961, p. 27). All samples were analvzed by the semiquantitative spectrographic method in addition to the above.

Comparative data determined as noted above and by the six-step spectrographic method are given in tables 8 and 9, where spectrographic data are compared with data determined by other methods for beryllium, tin, tungsten, copper, lead, and zinc. Data obtained by different methods used on these samples (tables 8, 9) generally correspond closely and show that semiquantitative spectrographic analyses are reliable for use in geologic studies.

DATA PRESENTATION

TRACE ELEMENTS IN MAGMATIC ROCKS AND MINERALS

As the tin deposits are associated spatially and genetically with small stocks of biotite granite that occur at six widely spaced localities on the western Seward Peninsula, samples of each granite were collected and investigated in detail by bulk chemical analyses (table 2) and by spectrographic analyses of individual minerals or gravity fractions (table 3). Of the six granite stocks analyzed, those at Cape Mountain, Ear Mountain, Brooks Mountain, and Black Mountain are porphyritic coarse-granite biotite granite with phenocrysts of

TABLE *2. Chemical composition of granites*

[Analysts: samplesl-5 (rapidi.rock method), P. L. D. Elmore, S. D. Botts, O. W. Chloe, Lowell Artis, H. Smith; sample 6 (standard method), Cyrus Feldman. Samples 1-5 are bulk chip samples; sample 6 is a chip sample]

ortlioclase that range from 1.5 inches in length at Brooks Mountain to not more than 0.75 inch at Black Mountain. Most of these stocks of coarse-grained granites are less than a mile in diameter, and all show faint marginal chilling as well as minor variations, such as local tourmalinization. The granites at the Tin Creek and Lost River localities are medium grained and nonporphyritic; that at Tin Creek is silicified along joints, and that at Lost River is sericitized. Both of these granites are locally converted to sulfide- and cassiterite-bearing quartz-topaz greisen. Greisen or unusual variants were not included in the bulk analyses.

The granites intrude the pre-Ordovician slate, phyllite, argillaceous limestone and graywacke, and the overlying carbonate rocks of Early Ordovician age. In slates, granites are bordered by biotite-andalusite hornfels which locally contains abundant tourmaline. In limestone, granite is bordered by medium- to coarse-grained marble that is irregularly converted to contact rock composed principally of vesuvianite (idocrase), garnet, fluorite, and tourmaline. The amount of contact rock varies considerably; for example, the granite at Brooks Mountain is bordered by as much as several hundred feet of vesuvianite, whereas that at Lost River (the main tin lode area) has contact rock only along mineralized fractures.

As the known beryllium lodes occur only in the Lost River area (fig. 1), which also contains the main lode tin deposits, the data in all the following tables were obtained from rocks in this general area. The trace-element content of selected sedimentary and metamorphic rocks from this area is shown in table 4.

After (and possibly during) the injection of the granite stocks in the Lost River area, numerous dikes were intruded, generally along fractures of a strong system striking N. 65° -85° E. across the Lost River area. The dikes consist of a complex group of dark rocks, generally with chilled borders, of lamprophyres characterized by a large amount of xenocrysts and xenoliths derived from granite, and of light rocks of granitic composition. The lamprophyres contain granite xenoliths, but no granitic dikes are known to contain lamprophyre xenoliths, indicating that the lamprophyres are the younger. As several light and dark dikes cut exposed granites, most dikes probably are younger than granite. These dike rocks have previously been described in detail (Sainsbury, 1965b),.and table 5 shows their content of trace elements, including nickel, chromium, and titanium because these elements are normally present in much smaller amounts in quartz-bearing rocks. The presence of these elements in the lamprophyres supports the conclusion that the lamprophyres originated by granitic contamination of mafic rocks originally of diabasic composition. The table also shows the trace-element content of two metasomatized dikes near the Lost River tin mine (61-ASn-180, -188) which have been largely replaced by adularia.

TABLE 3.—Trace-element content, in weight percent, of granite stocks and their constituent minerals TABLE 3. *Trace-element content, in weight percent, of granite stocks and their constituent minerals*

[0, below detection limit shown in table 1 except as indicated by footnote. Type of analysis: A, quantitative spectrographic, by J. C. Hamilton and H. V. Bastron;
B, semiquantitive spectrography J. C. Hamilton] [0, below detection limit shown in table 1 except as indicated by footnote. Type of analysis: A, quantitative spectrographic, by J. C. Hamilton and H. V. Bastron;

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Arithmetic calculations, above samples

ı For total rock analysis, see table 2.
1 Data are total rock analysis of 100-to 160-pound composite sample representing a large number of samples.
3 Data are from analysis of 100- to 160-pound composite sample representin

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 T ABLE $4. - T$ race-element content, in weight percent, of selected sedimentary and metamorphic rocks

(0 indicates the element was below the following detection limits, in percent: Be, 0.001; W, 0.01; B, 0.02; B, 0.001; Zn, 0.02; Nb, 0.001. W and Zn were tested for but were been been been as the following detection limits

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TABLE 5.—Trace-element content, in weight percent, of dike rocks (Type of analysis: A, quantitative spectrographic, B, semiquantitative spectrographic. Analysis: A, quantitative spectrographic, B, semiquantitative spectro [Type of analysis: A, quantitative spectrographic; B, semlquantitative spectrographic. Analyst, J. C. Hamilton] TABLE 5. *Trace-element content, in weight percent, of dike rocks*

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TRACE ELEMENTS IN METASOMATIC **ROCKS** AND MINERALS

After the injection of the granite stocks and dikes, ore deposits of tin, tungsten, and beryllium were formed. The tin deposits mainly are localized near or in granite, generally along tabular veins that follow faults or dike walls. Most of the exposed beryllium lodes are localized in shattered limestones beneath thrust faults, generally where dikes intrude the faults, or, as at Tin Creek, near exposed granite which is cut by lamprophyre dikes. Detailed studies in the Lost Eiver area (Knopf, 1908; Sainsbury, 1963, 1964b, 1965b) indicate that the ore deposits of beryllium are zoned around the tin deposits. The zonation is schematically shown elsewhere (Sainsbury, 1965b), and the main chemical changes in the formation of beryllium lodes from limestone are shown in table 6. The main chemical changes during formation of the quartz-topaz greisen tin ores have been summarized previously (Sainsbury, 1960, p. 1492).

For this study, pure minerals were separated from contact rocks and lodes by the methods described on page F5 and were analyzed for the specific elements (table 7) in order to trace them through the metasomatic cycle.

	1		$\overline{2}$			Gain $(+)$
Constituent	Weight percent	Grams per 100 _{cc}	Weight percent	Recalcu- lated to 100 percent	Grams per 100 _{cc}	or loss $(-)$ (grams per 100 cc
SiO_{2-1} Al_2O_{-} ---------- $Fe2O3$ FeO ------------- MgO ₋₋₋₋₋₋₋₋₋₋₋₋ CaO ₋₋₋₋₋₋₋₋₋₋₋₋₋₋ $Na2O2$ K_2O_{-} ------------ $H_2O + \ldots$ H_2O – $TiO2$ P_2O_6 ------------- MnO $CO2$ ------------ Cl_{2} , $\frac{1}{2}$, $\frac{1}{2}$ ${\bf F}_{-}$	7.35 2.15 . 39 .58 2, 03 47.67 . 05 . 42 .51 . 09 .10 . 03 . 02 38.30 . 01 . 05	19.85 5.81 1.05 1.57 5.48 128.71 .14 1. 13 1.38 . 24 .27 . 08 . 05 103.41 . 03 . 14	14.64 18.55 . 70 .22 1.60 40.02 1.35 1.21 2.07 . 12 . 06 . 01 . 14 . 16 00 27.00	15.18 19.24 .73 . 23 1.66 41.50 1.40 1.25 2.15 . 12 . 06 . 01 . 14 .17 00 27, 99	49.34 62.53 2.37 .75 5.39 134.87 4.55 4.06 6.99 . 39 . 19 . 03 .46 .55 00 90.97	$+29.49$ $+56.72$ $+1.32$ $-.85$ $-.09$ $+6.16$ $+4.41$ l, $+2.93$ $+5.61$ $+.15$ $-.08$ $-.05$ $+, 41$ -102.86 —. 03 $+90.83$
$Subtotal$ ₋₋₋₋₋₋₋₋ Less ------------- $Total$	99.75 .02 99.73	269.34 . 05 269.29	107.86 11.37 96.49	111.83 11.79 100.04	363.44 38.31 1325.13	$+198.03$ -142.27
					$ 2-269.29 $ $+55.84$	$+55.76$

TABLE 6. *Chemical changes in conversion of limestone to fluorite-beryllium ore* [Analysts: C. L. Parker, limestone; E. S. Daniels, ore, U.S. Geol. Survey]

1 Mass of sample 2 (weight percent X specific gravity). 1 Mass of sample 1.

SAMPLE DATA

1. Lab. No. D100123, field No. 62-ASn-RR23; sample type, argillaceous limestone, bulk chip; sp gr, 2.70. 2. Lab. No. D100397, field No. 62-ASn-RRl; sample type, ore, bulk chip; sp gr, 3.25.

TABLE 7.—Trace-metal content, in weight percent, of minerals from contact rocks, beryllium-fluorite ores, and tin ores

[0, below detection limit shown in table 1; nd, not determined. Type of analysis: A, quantitative spectrographic; B, samiquantitative spectrographic. Analyst. J. C. Hamilton]

GEOCHEMICAL CYCLE OF TRACE ELEMENTS

 $\frac{1}{2}$ in oblique reflected light, shows both clear grains and curdy amorphous grains.
 $\frac{1}{2}$ Handpicked fragments of small (2–3 mm) enhedral crystals. No polished section \overline{a} ٩ sion oil.

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TRACE ELEMENTS IN STREAM SEDIMENTS, SOILS, PLANTS, AND WATER

The behavior of trace elements in supergene processes was investigated by use of stream sediments, soil and plant samples, and, for beryllium, water.

Stream sediments. Several hundred stream-sediment samples wereanalyzed during the study, but only a few representative ones are shown in table 8. These were selected as representative of those from diverse geologic terranes, both mineral bearing and barren. In tables 8-11, elements are reported in parts per million to conform to usage in the literature on geochemical prospecting, where most such analyses appear. Table 8 also compares results of different analytical methods for beryllium, tin, and tungsten.

/Soils and plants. Soil and plant samples were taken across the mineralized zone in the Lost River valley (pi. 1) by the methodsdescribed on page F5. The mineralized zone is coextant with the Rapid River fault and consists of both tin deposits characterized by stannite and silver-bearing sulfides and the usual fluorite-beryllium ores. Table 9 gives the trace-element content of soils; tables 11 and 12 give the changes in trace-element content, relative to the underlying soil, of plant ash from bulk tundra clumps and from individual plants and lichens separated from tundra clumps.

TABLE 8. *Trace-element content, in parts per million, of selected stream sediments* TABLE 8. - Trace-element content, in parts per million, of selected stream sediments [0, below detection limit shown in table 1] [0, below detection limit shown in table 1]

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z Semiquantitative spectrographic analyses, by J. C. Hamilton, R. G. Havens, and Barbara Tobin.
* Determined spectrophotometrically by dithiol method after separation of tin by distillation, by Dorothy Ferguson and Claude 3 Determined spectrophotometrically by dithiol method after separation of tin by distillation, by Dorothy Ferguson and Claude Huffman, Jr. 4 Determined spectrophotometrically, by Dorothy Ferguson and Claude Huffman, Jr.

' Barely detected; concentration uncertain.

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TABLE 10. *Trace-element content in rocks and soils, Lost River valley*

[All values In parts per million. Analyst, J. C. Hamilton]

1 Arsenic is not included because detection limit is too high for comparison; lithium not included because spectrographic data are not certain.
 $\sqrt[2]{\text{No}}$ data; detection limit too high for comparison.
 5 In round

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[N.C. Indicates that element was unchanged in concentration; X , that element was below the detection limit in both soil and plant ash. Plus (+) prefix indicates that the plant ash contained greater amounts of the elemen [N.C. Indicates that element was unchanged in concentration; X , that element was below the detection limit in both soil and plant ash. Plus (+) prefix indicates that the plant ash contained greater amounts of the element than did the soil, and the value given is the difference, in parts per million, between these two amounts; minus (--) prefix in-
ash contained greater amounts of the element th dicates the opposite. Analyses, by semiquantitative spectrographic method, by J. G. Hamilton and Barbara Tobin]

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GEOCHEMICAL CYCLE OF TRACE ELEMENTS

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[X indicates that element was below the detection limit in both soll and plant ash; N.C. that element was unchanged in concentration. Plus $(+)$ prefix indicates that the plant ash contained greater amounts of the element adicates that element was below the detection limit in both soil and plant ash; N.C. that element was unchanged in concentration. Plus (+) profix indicates that the plant
ash contained greater amounts of the element than d the opposite. Analyses, by semiquantitative spectrographic method, by J. C. Hamilton and Barbara Tobin]

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DISCUSSION

GRANITES

The data presented in table 13 suggest that the granites of the Seward Peninsula, compared with some other tin-granites, are considerably enriched in beryllium, are slightly lower in niobium, and contain about equal amounts of the other elements listed. The granites can, then, be considered as normal tin-granites, possibly enriched in beryllium. Direct comparisons could not be made for all elements because data on all elements from a similar geologic terrane were not available. Additional comparisons are presented in table 14. Because the trace-element content of minerals investigated varies widely, the ranges, rather than the averages, are compared because averages can hide major variations.

TABLE 13. *Trace-element content, in parts per million, of granites from the Seward Peninsula compared with that of other granites of tin-bearing regions or with other biotite granites*

Element	Seward Peninsula ¹	Other regions ²	Source of data		
Be_{-} Be --------- $Be_{\texttt{2}}$ Sn_{max} Li. $B_$ Nb_{2} Cu_{2} Pb \mathbb{Z} n - - - - - - - - - $\mathbf{z}_{\mathbf{n}}$	$4 - 16$ $8 - 35$ 65–270 40–300 $25 - 65$ $6 - 70$ $30 - 60$ 300	(T) 4 (A) $0 - 30$ (T) $4 - 9$ (T) $4 - 45$ (T) 400 (T) 275 50–275 (A) (A) 10 40 (T) (T) $5 - 34$ (A) $5 - 120$	Beus (1962, p. 26). Shawe and Bernold (1964). Chauris (1965, p. 70). Rattigan (1963, p. 139). Butler (1953, p. 159). Butler (1953, p. 160). Butler and Smith (1962, p. 950). Turekian and Wedepohl (1961). Butler (1953, p. 160). Ottemann (1941). Wedepohl (1953, p. 119).		

' Range of values from table 2. 1 T, granites of tin-bearing regions; A, other biotite granites.

Biotite. All biotites were enriched in tin, zinc, and niobium; beryllium, boron, lead, and copper were present in approximately the same concentration as in the bulk granites. This distribution is not unusual except possibly the great enrichment in zinc. The single bleached biotite from the granite at Lost River was enriched in boron and lithium, reflecting the initial stages of its conversion to lithium-bearing white mica, but the content of other trace elements remained about the same. Even though the tin content of all biotites is high, it is still well below that in some muscovite micas from pegmatites which, according to Ahrens and Liebenberg (1950, p. 575), contain as much as 0.013 percent $SnO₂$ (about 0.010 percent Sn).

Quartz. As expected, the trace-metal content of quartz is low; the higher values are suspect because of the slight amount of plagio-

TABLE 14.—Selected trace-element contents, in parts per million, of minerals in granites of the Seward Peninsula compared with corresponding
TABLE 14.—Selected trace-element content granites from tin belts or with those in

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a Valus ch^{oot}, "2015", 21 in blotte reported here are marked (A) granite, but the Payson Granite contains 230 ppm Sn in altered blotite, indicating this granite may be a "ting falles".
granite."
* Contains minute needles

clase that could not be separated. The quartz samples from the granites of Brooks Mountain and Black Mountain are virtually pure, and the total trace-metal content is low. As shown in table 14, the tracemetal content of quartz from other granites generally is also low.

Plagioclase. The literature contains conflicting data on the tin content of feldspars from tin-granites. Jedwab (1953) found that feldspar rather than muscovite carried the highest tin values in tinbearing pegmatites. Kattigan (1963) found less than 5 ppm tin in feldspars from the Australian tin-granites. The three plagioclases from different granites on the Seward Peninsula are enriched in tin to a degree, but are impoverished in copper, niobium and boron; the beryllium and lead contents of the plagioclases are equivalent to those of the whole rock.

Orthoclase. - Orthoclase is enriched in tin but is impoverished in beryllium, copper, niobium, and boron when compared with the granites as a whole. Values of all elements are within or close to ranges reported for other regions.

Heavy-mineral fraction. Perhaps the most striking feature shown in table 3 is the great enrichment of all the elements, lithium excepted, in the heavy -mineral fractions from three granites. Beus (1962, p. 28- 30) has shown that some accessory minerals of granite, such as allanite and eudialyte, are enriched in beryllium, and Oftedal (1961) showed that tungsten is detectable in Norwegian granite-pegmatites only in the accessory heavy minerals. In the Seward Peninsula, detectable tungsten is limited to the heavy-mineral fraction (the detection limit is high at 100 ppm). Although the amount of heavy minerals that have a specific gravity greater than 3.3 is so low in the granites that it cannot account for a large share of the trace metals, the very large concentration ratios would seem to indicate that this fraction would be valuable in geochemical exploration. These results are directly opposed to results obtained by Ottemann (1941, p. 156) on tinrich granites from the Harz Mountains, Germany, where the heavy minerals with higher specific gravity than Clerici solution $(3.5-4.9)$ contained less tin than did the granite as a whole.

DIKE ROCKS

The trace-element content of the dike rocks (table 5) is compatible with the assumption that the lamprophyres originated by contamination of diabase by granitic rocks. In particular, there is a general inverse relation between beryllium and tin and copper, nickel, chromium, and titanium, two groups that are characteristic of granites and mafic rocks, respectively. The lamprophyres, which are hybrid rocks, contain both groups, and xenocrysts separated from one lamprophyre (63-ASn-656) contain trace elements in amounts roughly equivalent to those in similar minerals from the granites. The metasomatized cassiterite dike contains a highly anomalous amount of tin and, thus, clearly shows the passage of tin-rich solutions.

CONTACT ROCKS

MINERALS FROM SKARNS

Pure vesuvianite and garnet from contact rocks were separated and analyzed to provide data comparative with those for similar minerals from Iron Mountain, N. Mex., and elsewhere. As noted by many workers, vesuvianite may contain as much as 3.95 percent BeO. (See Warner and others (1959, p. 17-18) for summary.) Vesuvianite at Iron Mountain, where the beryllium mineral helvite occurs in skarns that contain the vesuvianite, contains 1.09 percent BeO (Jahns, 1944). Silbermintz and Eoschkowa (1933) believed, however, that pure vesuvianite will not accept such large amounts of beryllium. The analyses of vesuvianite from the Seward Peninsula, showing a BeO content of only 0.05 and 0.005 percent, support this belief. Grossularite garnet from Iron Mountain, N. Mex., contains BeO in the range of 0.08-0.19 percent, much higher than that of the single garnet analyzed from Tin Creek. Even though numerous veins and veinlets of fluorite beryllium rock, as well as small amounts of helvite-bearing skarn ("ribbon rock"), occur near the granite at Tin Creek, very little beryllium entered the lattice of vesuvianite and garnet. Most of the beryllium deposits formed during a later stage of mineralization, and the earlier beryllium principally formed helvite.

MINERALS FROM ORES

Owing to the coarse grain size of the minerals in the tin ores, pure fractions of several minerals could be easily prepared. With the exception of the arsenopyrite, for which no polished section was prepared, the minerals from the tin ores shown in table 7 were extremely pure, and the trace-element content of most is low.

In the fluorite the tin content is high and the beryllium content is low, reflecting deposition in an environment where tin was being deposited in large amounts. Only a few determinations of tin in fluorite have been published, and in these the tin ranges from zero (Borchert and Dybek, 1959-60, p. 141; Barsukov and Pavlenko, 1956) to 1 ppm (Ottemann, 1941, p. 162). None of these are from tin ores, as are the determinations of the samples reported on here. Eecent work by Waters, Burton, Clements, Lovesey, and Morris (1965, p. 1297) shows that fluorites from various tin-bearing areas contain no more than 11 ppm beryllium but that many contain more than 5 ppm. These

authors show that fluorite precipitated from beryllium-rich solution can contain as much as 900 ppm beryllium (p. 1299). The low beryllium content of the two fluorites listed in table 7 possibly is a function not of a low concentration of beryllium in the solutions but of the exclusion of beryllium from the fluorite by tin, which is present in large amounts.

Both fluorites contained, in addition to the elements reported in table 7, Si, Al, Fe, Mg, Mn, Cr, Sr, Ce, and Y, 'and one also contained Ag, Ba, Bi, La, and Yb. Alien (1952, p. 920) noted that most fluorites tested by him contain Mg, Al, Mn, Sr, and Y, and that their common trace elements are Be, Ag, Ba, Yb, and Pb.

In the arsenopyrite the trace elements are those most easily explained by minute inclusions of other sulfide minerals. In addition to those elements shown in table 7, the arsenopyrite contained the following elements, in parts per million: Si, 15,000; Al, 3,000; Mg, 300; Ca, 2,000; Ti, 300; Mn, 15; Ag, 20; Ba, 2; Bi, 200; Co, 150; Cr, 3; Ga, <20; Mo, 15; Ni, 30; Sb, 1,500; V, 15; and Zr, 10.

The two topaz samples analyzed (table 7) had tin, copper, and lead as common elements and had the following contents of other trace elements, in parts per million: Fe, 3,000 and 500; Mg, 100 and $\lt 50$; Ca, 3,000 and 700; Ti, 70 and 50; Mn, 50 and 30; Ba, 3; Co, 0 and 3: $Cr, 2$ and 3 ; $Ga, 30$ and 15 ; $Ge, <50$ and $₅₀$; $Tl, 1,000$ and 700 ; $Y, 30$ </sub> and 0; Yb, 5 and 1; Sc, 7 and 0; Zr, 10 and 10. Of these elements, the germanium and relatively high thallium are of interest because these elements are generally present in smaller amounts.

The trace-element content of cassiterite has been discussed in many publications (see Borisenko and Lizunov (1959) for a summary of 300 analyses), and certain colors of cassiterite have been correlated with certain trace elements .The rare-element content of dark cassiterite from the Lost Kiver tin mine is compared with that of almost colorless cassiterite from Cape Mountain (color almost identical with that of scheelite) in table 7. The major difference is the very high tungsten and iron content of the dark cassiterite. In addition, the dark cassiterite contains the following elements, in parts per million, that are not found in the light cassiterite: Ga , <30 ; and Ni, 5; trace elements common to both are, in parts per million (dark first) : Si, 10, 500; Al, 300 and 200; Mg,<50.and 200.; CA, 700 and 1,000; Ti, 500 and 700; Ba, 2 and 2; Cr. 1.5 and 1; Sc, 15 and 5; V, 15 and 20; Zr, 50 and 30. Submicroscopic inclusions of wolframite can possibly account for both the dark color and the high iron and tungsten content of the dark cassiterite, as was proved for some cassiterites by Grigorev and Dolomanova (as quoted by Borisenko and Lizunov, 1959). The ubiquitous presence of zirconium, aluminum, iron, manganese, titanium, and silica

in cassiterites of all origins was established by Borovik and Gotman (1939).

Owing to the very fine grain size of the ores, which required the grinding of material to less than 300 mesh in size, the purity of the minerals separated from the beryllium ores is suspect, and the beryllium values given in table 7 can be considered maximum. Of these minerals, the tourmaline, mica, and diaspore apparently accepted large amounts of beryllium. Tourmaline may contain as much as O.OX percent BeO (Warner and others, 1959, p. 36; Beus, 1962, p. 36), but analyses of tourmaline from beryllium ores comparable to the Seward Peninsula ores are not available. We have found no analyses showing the trace-element content of hydrothermal diaspore. Micas from pegmatites were found by Goldschmidt and Peters (1932, p. 366) to contain as much as O.OX percent BeO, and Beus (1962, p. 36) stated that lepidolite and muscovite from pegmatites may contain as much as 0.0126 percent beryllium. Also, mica that contains as much as 3 percent BeO has been synthesized by Eitel, Hatch, and Humphrey (1950). In this synthetic mica, Be⁺²Si⁺⁴ substitutes for Al⁺³Al⁺³ in tetrahedral coordination. As the diaspore, tourmaline, and mica discussed here grew in a high-temperature solution saturated with beryllium, their contents of 0.7, 0.3, and 0.07 percent BeO may be maximum for these minerals in natural occurrences. The tourmaline is colorless, shows no absorption or dichroism, and has indices of refraction E=1.624, $O=1.637\pm0.005$. The tin content of these purified minerals is higher than that of similar minerals, not from tin veins, reported by Borchert and Dybek (1959-60, p. 141). The content of other trace elements, especially niobium, is relatively low.

RARE ELEMENTS IN STREAM SEDIMENTS, SOILS, PLANTS, AND WATER

During the weathering and decay of the granites, lodes, and contact rocks, clear-cut geochemical anomalies were formed in stream sediments, soils, and plants of the area. In the initial stage of this study, a reconnaissance of the granites of the western Seward Peninsula showed anomalous beryllium content in stream sediments around the .granites, and use of these data contributed to the discovery of large beryllium lodes (Sainsbury, 1963, p. 12-15).

STREAM SEDIMENTS

In this report of Sainsbury (1963, p. 12-16), the maps show the beryllium content of stream-sediment samples from different areas in the western Seward Peninsula. From these and other samples collected since 1960, it has been determined that the beryllium content of total stream sediments less than 40 mesh in size varies greatly with the rock type within the drainage basin of the streams. In limestone areas, the background content of beryllium probably does not exceed 1.5 ppm and definitely is below 3 ppm. Where granite underlies a substantial part of the drainage basin, the beryllium content of stream sediments may approximate that of the granite (as much as 18 ppm). Hence, a value that definitely is anomalous in one area is not anomalous in another, and these differences should be kept in mind during geochemical prospecting.

In limestone areas a beryllium content in the range of 3-5 ppm might be termed the "threshold" value, and beryllium in the range of 5-10 ppm definitely is anomalous. The maximum values to be expected in sediments will, of course, be a function of the size of the drainage basin, of the amount and richness of ore bodies exposed at the surface within the basin, and of their nearness to the stream. An upper value to be expected in the Seward Peninsula, and probably elsewhere in the Arctic and sub-Arctic, where mechanical distintegration predominates over chemical decay, should approximate the values obtained in Camp Creek, where a long and continuous lode system crops out in the small drainage basin. In this small stream the maximum amount of beryllium in total stream sediment was 160 ppm, and in all samples the amount exceeded 100 ppm. Large and small boulders of fluorite-beryIlium rock form a significant proportion of the bed load, and these boulders contain beryllium in the range of 0.2-1.75 percent BeO.

In Tin Creek, a larger stream that contains both granite and beryllium-fluorite lodes within its drainage basin, sediments contain beryllium in the range of 10-30 ppm; the highest value was found in sediments downstream from the area of marble that contains numerous veinlets of fluorite-beryllium rock.

In Rapid River valley, where a mineralized belt in limestone crosses the stream, sediments contain as much as 16 ppm beryllium, but values decrease rapidly to less than 3 ppm within a mile downstream.

Stream sediments from the east headwaters of the Mint River, which drains the southwest margin of the granite of Brooks Mountain, consistently contain more than 13 ppm beryllium, yet careful search has failed to find significant fluorite-beryllium lodes. The apparent anomaly is explained by the large amount of granite in the stream sediments and by the fairly large volume of vesuvianite from the contact zone of the granite. The granite contains 15 ppm beryllium, and the vesuvianite as much as 50 ppm beryllium.

The form in which the beryllium is transported has not been determined. Near lodes, discrete fragments of ore can be found, but because of the softness and friability of the fluorite, the ore breaks apart readily. Diaspore and chrysoberyl, however, are both hard and chemically resistant, and discrete fragments of these materials have been found in sediments well downstream from the lodes. If these fragments persist for long distances, a technique suggested by Vance Kennedy (oral commun., 1964) might extend the distance over which beryllium anomalies could be recognized in limestone areas. Kennedy suggested that acid leaching of the carbonate fraction of sediments would enrich the residue in beryllium to such an extent that beryllium present in amounts well below 1 ppm could be detected by use of the morinfluorescence field method (Patten and Ward, 1962). This suggestion has merit.

To determine the geochemical association of trace elements in sediments, more than 100 samples were analyzed for beryllium, tin, molybdenum, and tungsten; 17 of these samples, which are representative of the 100 samples, were analyzed by semiquantitative spectrographic analyses for many elements (table 8). The trace elements that are associated in the igneous rocks and in the tin and beryllium lodes are also associated in the stream sediments, except that zinc and niobium are quickly reduced below their detection limits. A direct correlation exists between tin, tungsten, arsenic, and lead. Although most samples high in tin and tungsten contain anomalous amounts of beryllium, the highest values for beryllium are from samples that contain less than the maximum amounts of tin, tungsten, lead and arsenic. This follows as a result of the zonal distribution between the tin-tungsten-basemetal lodes and the beryllium-fluorite lodes; beryllium-rich detritus was shed into some drainages-for example, Camp Creek-whereas tin- and sulfide-rich detritus was shed into other streams-for example, Cassiterite Creek.

SOILS

To determine the applicability of geochemical sampling of soils as a method of prospecting for beryllium lodes, soil samples were taken in the Lost River valley along two traverse lines that cross the mineralized zone which lies along the Rapid River fault. Control samples were taken far from mineralized areas to establish background values. In the Lost River valley, bedrock along the traverse lines is veneered by frost-broken limestone bedrock, upon which a thin residual soil is developing. Clumps of tundra vegetation cover possibly 30-50 percent of the ground surface, and between the clumps the soil has a veneer consisting of yellow to reddish clay and limestone pebbles. Beneath the clay and pebble zone, yellowish clayey soil 1-2 inches thick overlies frost-broken bedrock. All the soil samples came from the yellow clay zone, in which there are no pebbles. A sample of the vegetation mat was taken from the tundra nearest each soil-sample locality, generally

within 2 feet of it. The locality of soil samples and the contents of beryllium, copper, lead, zinc, and tin in the samples are shown on plate 1. The control samples were collected in the area around the mouth of Esch Creek, which flows west into the Lost River about 1 mile north of the area shown on plate 1; their metal content and the analytical method used are given in table 9.

The data given in tables 4 and 9 are summarized in table 10 to show the background value and maximum enrichment factors in soil during weathering. As the soil samples consist principally of clay, most of the metals probably are held in the interlayers of the clay minerals, a relation found to be common (Beus, 1962, p. 41; Warner and others, 1959, p. 28). The heavy-metal anomaly is broad along the east side of Lost River, where the remnants of a thin mantle of glacial drift contain mineralized rock from the Lost River tin and beryllium deposits and where the mineralized Rapid River fault swings north (pl. 1) along the valley. The anomaly is narrower on the west side of the valley, where the mineralized zone along the Rapid River fault is perpendicular to the valley and where glacial drift is lacking. As shown in table 10, except for tin, the background value of soil exceeds that of limestone bedrock, and the enrichment factors of tin and beryllium are very high. The degrees of copper, lead, and zinc enrichment are comparable to those of other areas, and residual clay soil is but slightly enriched in boron and niobium. Vinogradov (1959) showed that clayey soils are strongly enriched in beryllium, and Warner and others (1959, p. 19) pointed out that most hydrothermal clays contain detectable amounts of beryllium.

The niobium content of the soils in Lost River valley is similar to that of lateritic soils from West Africa, which contain an average of 24 ppm niobium (Grimaldi and Berger, 1961) in unmineralized areas and as much as 87 ppm in soils within a few miles of a known deposit of niobium.

PLANTS

Most of the study area is sparsely covered with low-growing tundra vegetation; trees and tall shrubs are absent. Clumps of tundra vegetation that form tough mats cover about 40-60 percent of the soil but only a small percentage of rock outcrops. The ability of plants to concentrate certain elements in their tissue and release them to the soil during decay is well known (Hawkes and Webb, 1962, p. 290-305). In many vegetated areas, the decay of plants is a factor in the development of geochemical anomalies. To assess the role of plants in the geochemical cycle and in the formation of soil anomalies, representative plants were collected at or near each station where soil samples were collected.

Only a few analyses of plants for certain elements have been published, and still fewer analyses have been reported for tundra plants. Beus (1962, p. 42) noted the paucity of information on the beryllium content of plants and suggested that more data are needed. Hawkes and Webb (1962, p. 359-377) cataloged the geochemical characteristics of 33 elements but gave the biological responses and amounts in plant ash for only 16 of these elements. Because of the lack of guidelines, the element content of individual plant species could not be designated as falling into the background or the anomalous ranges of certain elements. However, the element of the plant ash could be compared with that of the soil on which the plants grew, and the role of the plants in enriching soil could be determined, as is shown in tables 11 and 12.

In some tundra clumps the plants were separated by species and were analyzed to determine if certain plants preferentially enriched certain elements. The plants were identified by H. T. Shacklette, botanist, U.S. Geological Survey. The tundra clumps in Lost River valley consist mostly of *Arenaria arctica,* but they also have minor amounts of other species. The following plant species were segregated from the tundra clumps and analyzed: Six herbaceous flowering plants, *Arenaria, arctica* Stev., *Eretricfwum aretioides* (C. & S.) DC., *Dryas integrifolia* Vahl., *Saxifraga eschscholtzii* Sternb., *S. oppositifolia* L., and *Silene acaulis* L.; three mosses, *Drepanocladus fluitans* (Hedw.) Warnst., *D. uncmatus* (Hedw.) Warnst., and *D.* sp.; and one lichen, *Thamnolia vermicularis* (Sw.) Ach. The nomenclature follows Anderson (1959) for the flowering plants; Crum, Steere, and Anderson (1965) for the mosses; and Hale and Culberson (1960) for the lichen.

Owing to the high winds and heavy rains which periodically coat the tundra plants with soil, much soil is permanently fixed to the growing plants. Even after repeated washings and massagings in distilled water, minute fragments of minerals could be obtained from many of the plants. Hence, the quantitative enrichment of trace elements in plants was impossible to determine. However, in tables 11 and 12 the rare-element content of the ash is shown as the change, in parts per million, of the trace-metal content compared with the content of the soil on which the plant grew. Obviously, if the content in the ash exceeds the content in the soil, the plant has concentrated that element. Mitchell (1960, p. 555) stated, "The permissible limit of contamination for any element depends on the ratio of its contents in the sample and in the contaminant, not on its absolute amount in either. * * * It is only for elements with ratios [soil/plant, dry weights] above 100 that due regard must be paid to the possibility of soil contamination in considering the accuracy of analytical results."

Aluminum is one of the elements that commonly is more abundant

in soils than in plant ash; therefore, the ratio of aluminum in the soil to aluminum in the ash is given in table 10. Where the ratio exceeds 1, soil contamination cannot have had a large effect in contributing rare elements to the ash. Furthermore, aluminum is a characteristic element of most plants (Wallace, 1961) and the alumina in plant ash may not be a result of contamination at all. Shacklette (1965, p. D11, D17) reported that the ash of one moss sample contained 45 times more aluminum than did the substrate of the moss; however, some moss samples contained less aluminum than did their substrates.

The data presented in tables 11 and 12 demonstrate the following:

- 1. Several elements—principally copper, lead, and boron—are consistently enriched in the bulk tundra clumps and in specific plants. These elements are enriched in plants growing on soil that con- \cdot tains the elements in amounts below detection limit.
- 2. In most tundra clumps and in specific plants, silver was enriched and zinc was highly enriched.
- 3. Arsenic, beryllium, tin, and niobium tended to have lower concentrations in plant ash, although there were exceptions that are explainable for tin and, less so, for beryllium. When the data were plotted, there was a point at which tin systematically changed from apparent gain to apparent loss (negative value relative to the soil). Tables 10,11, and 12 show that as long as the concentration of tin in the soil is below about 100 ppm, the tundra plants enrich tin, but when the concentration in the soil exceeds 150 ppm, the concentration level in the plant is negative (shown by minus sign in the tables). The same relation is true to a lesser degree for beryllium, for if the soil content is at or below 20 ppm, the tundra plants enrich beryllium. If the soil contains more than 50 ppm beryllium, all the plants cannot absorb more than this; and as the concentration in the soil increases to high values, the tested plants show a negative value. The relations are shown in figure 2, in which any point to the right of the "no change" line is indicated in tables 11 and 12 by a prefix plus sign, and a point to the left by a minus sign.

Eomney, Childress, and Alexander (1962) demonstrated that beryllium in nutrient solution inhibited the growth of bush bean seedlings, caused early flowering, and led to enrichment in beryllium of parts of the plants, notably roots. The highest concentration of beryllium in the dry plant (roots) reached 1,076 ppm in solutions with 5 ppm beryllium in soluble form. Zalashkova, Lizunov, and Sitnin (1958) showed that both soils and certain plants over beryl-bearing pegmatites contain anomalous amounts of beryllium. In plants, the highest value obtained was 39 ppm beryllium in ash from alder

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FIGURE 2.-Relation between content of beryllium and tin in plant ash and in underlying soils. Areas enclosed by each line contain at least 90 percent *of* the samples analyzed.

leaves. W. R. Griffitts (oral commun., 1965) found that plants growing over beryllium deposits at Spor Mountain, Utah, and at Aguachile, Mexico, concentrated beryllium up to a maximum of 150 ppm in ash.

Along Lost River, the concentration of beryllium in plants reaches 150 ppm in ash of *Sawifraga,* a value comparable to the greatest enrichment found by Griffitts but considerably less than that in the cultured bush beans. Although identical species are not available from diverse areas, the major factor in enrichment of beryllium is probably the form in which the beryllium occurs around the plant roots. The concentration of beryllium in soluble form in natural soil water is presumably less than the 5 ppm in solutions used by Romney, Childress, and Alexander (1962).

4. The single lichen investigated *(Thamnolia vermicularis*, a long, wormlike white lichen similar to that often referred to in Alaska as "Staghorn lichen") rejected all metallic elements except silver which it concentrated.

Boron, copper, and zinc are well established as essential trace elements in plants (for summary, see Wallace, 1961, p. 12-14), and hence their ubiquity is to be expected.

WATER

Only the beryllium content of clear water was investigated. The content of beryllium in waters free of colloidal material is very low (generally below 0.000001 percent) and well below the limits of detection by ordinary spectrographic procedures. However, as no analyses are reported for waters free of colloidal material from distinctly beryllium-rich deposits, several samples of clear water from Camp Creek, which contains a large number of boulders and cobbles of fluoriteberyIlium rock, were tested in the field by use of the morin-fluorescence method (Patten and Ward, 1962). Aliquots of water to 10 times the recommended sample weight were used in the analyses but no beryllium was detected, which suggests that the beryllium in solution in the water was less than 0.3 ppm (0.00003 percent).

SUMMARY

The geochemical cycles of the elements are summarized graphically on plate 2. From the data presented, the authors conclude that the biotite granites, as compared with the sediments they intruded, were enriched in the rare elements beryllium, tin, lithium, boron, copper, lead, zinc, and niobium. The lamprophyre dikes acquired beryllium through ingestion of granite. Within the granites, the distribution of trace elements generally parallels the distribution observed elsewhere. Even though the granites are abnormally rich in beryllium, however, the earliest tactites that presumably formed during the crystallization of the granites contain less beryllium than in tactites observed at other places-for example, at Iron Mountain, N. Mex.

The mineralizing stage followed the intrusion of mafic dikes which were low in silica and low in the trace elements that are common in granite, into fractures of a regional fault system that cut the exposed granites. A significant length of time must have elapsed between the consolidation of the exposed granites and the entrance of mineralizing solutions that formed the tin and beryllium ores. During this time, trace elements and volatiles presumably concentrated in deeper parts of the granites, and the faulting and entrance of the lamprophyre dikes fractured the cooled shell of the granite. This fracturing allowed the volatiles and trace elements to escape into the overlying rocks where significant ore bodies of tin, beryllium, and fluorite formed. The absence of pegmatites in the western Seward Peninsula indicates that little of the residual water and volatile-rich fluid that concentrated

during crystallization escaped to form pegmatites. The large amount of residual water and volatile-rich fluid remained to form a very volatile-rich residual phase. On the basis of Shawe and Bernold's suggestion (1964, p. B100) that the increased beryllium content of silicic rocks can be directly correlated with the depth of crystallization, the Seward Peninsula granites were possibly emplaced far below the surface.

Most of the rare elements that are associated in the granite stocks and in the ore deposits of the district retain this association throughout weathering and transportation of elements in supergene processes. Zinc may be an exception in that it occurs in relatively low concentrations in the stream sediments, although ferroan sphalerite is a common mineral in the tin deposits. A possible explanation is that zinc is highly concentrated in the plants and residual clay soil and, thus, is less available in the stream sediments that are within the size range generally sampled (less than 40 mesh). In spring and summer, during spring melting and in heavy rains, much of the residual clay soil is flushed to the ocean in high waters, and only a small percentage of the zinc-rich soil is left in the stream sediments.

The elements needed for plant growth (boron, copper, zinc) are concentrated in all plants; those without established use patterns (beryllium, niobium, tin) vary somewhat erratically, the concentration level generally being a function of the concentration in the soil. Niobium remains dispersed throughout the supergene cycle and shows no major concentration similar to that observed for the other elements investigated.

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