Copper Mosses as Indicators of Metal Concentrations

GEOLOGICAL SURVEY BULLETIN 1198-G

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By HANSFORD T. SHACKLETTE

CONTRIBUTIONS TO GEOCHEMICAL PROSPECTING FOR MINERALS

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A study of mosses that grow on substrates which contain large amounts of metals and the use of these plants in mineral prospecting

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ABSTRACT

Some mosses and liverworts are known throughout the world as indicators of sites of metallic enrichment, particularly of copper, in the substrates. These plants commonly have been designated "copper mosses" in the literature, and although the term is not entirely appropriate, it is used in this report. The copper moss *Mielichhoferia macrocarpa* grew in the Aleutian Islands on lithosol and volcanic rocks that contain amounts of copper, lead, and vanadium greater than the average amounts in mafic rocks, but amounts of manganese, nickel, and zinc less than the average. Growing adjacent to this moss was *Platydictya jungermannioides*, a species that is not considered by botanists to be a copper moss. The rock on which *Mielichhoferia* grew contained five times as much chromium and somewhat more iron, nickel, lead, titanium, vanadium, yttrium, and zirconium than did the rock on which *Platydictya* grew, although the two samples occurred less than a meter apart. The lithosol of the rock crevices which supported *Mielichhoferia* contained 10 times the average copper content of soils; that which supported *Platydictya* contained one-fourth less than was found in the *Mielichhoferia* substrate. Compared to the rocks, the lithosols contained the same amounts, or less, of the elements for which analyses were made, a fact which indicates that leaching of soils is active at this site. These data suggest that this species of *Mielichhoferia* is a copper moss, whereas *Platydictya* is not.

Chemical analyses of a copper moss are given. No significant difference exists in the element content of the two mosses that grew at this Aleutian Island site; both contain noteworthy concentrations of copper, boron, and vanadium, the element content being about 5, 10, and 14 times, respectively, the average amounts that are in mosses. The vanadium content of 0.1 percent in the two samples is probably the greatest concentration of this element that has been reported in any plant sample. The amounts of sulfur in the substrates of the copper moss are not large; this fact suggests that the metals, not the sulfur, control the occurrence of this moss.

The substrates of two other species of copper mosses from eastern North America and from Europe were analyzed and were found to contain much greater than normal concentrations of certain metals at two of three locations.

Reports in the literature indicate that the mosses *Merceya ligulata*, *M. latifolia*, and the liverwort *Gymnocolea acutiloba* grow most commonly or perhaps exclusively on substrates that are enriched in metals. These reports and the analyses of this study support the belief that knowledge of the occurrence of *Mielichhoferia* species and some other copper mosses can be used in prospecting for metals—habitats of museum-held specimens can be tabulated and these localities then examined by means of conventional prospecting methods.

INTRODUCTION

Several species of bryophytes (mosses and liverworts) have been known to grow on substrates (principally rocks) that have greater than the normal content of copper or other metals. Species having this substrate requirement or "preference" are known as copper mosses, although some are associated with metals other than copper and some are liverworts—not mosses. This report follows the established usage of the term "copper moss" even though this name often is inappropriate. Copper mosses are widespread in their distribution throughout the world, but are rare everywhere, a fact attributed to the general scarcity of outcrops of metallic minerals.

In November 1965, while studying the vegetation of Amchitka Island (Rat Islands group) in the Aleutian chain, Alaska, I discovered a colony of *Mielichhoferia macrocarpa* (Hook. ex Drumm.) Bruch and Schimp. ex Jaeg. and Sauerb. (fig. 1) growing on volcanic rock that probably is of early Tertiary age (Coats, 1956, p. 90 and pl. 17) near Cyril Cove on the Bering Sea coast. Plants of the genus *Mielichhoferia* are generally known as copper mosses; however, literature references to this species have not definitely associated it with mineralized substrates (Flowers, 1929, 1933, 1936; Andrews, 1932). Because of the uncertainty of its relationship to metals in the substrate and because it has been so infrequently discovered (Amchitka Island is the only Alaskan location where it is known to grow), I obtained samples of the lithosol from the rock crevices where it grew, of the volcanic rock, and of the moss itself for chemical analysis. In addition, I collected samples of the moss *Platydictya jungermannioides* (Brid.) Crum and its substrates even though *Platydictya* is not known as a copper moss. It was, however, the only other species of plant growing in the immediate vicinity of the *Mielichhoferia* colony.

This report gives the analyses of these as well as other samples of copper mosses and their substrates and, insofar as possible, compares these analyses with those published elsewhere. The worldwide occurrence of copper mosses is discussed, and special emphasis is placed on the species that are found in North America and their use in geochemical prospecting.

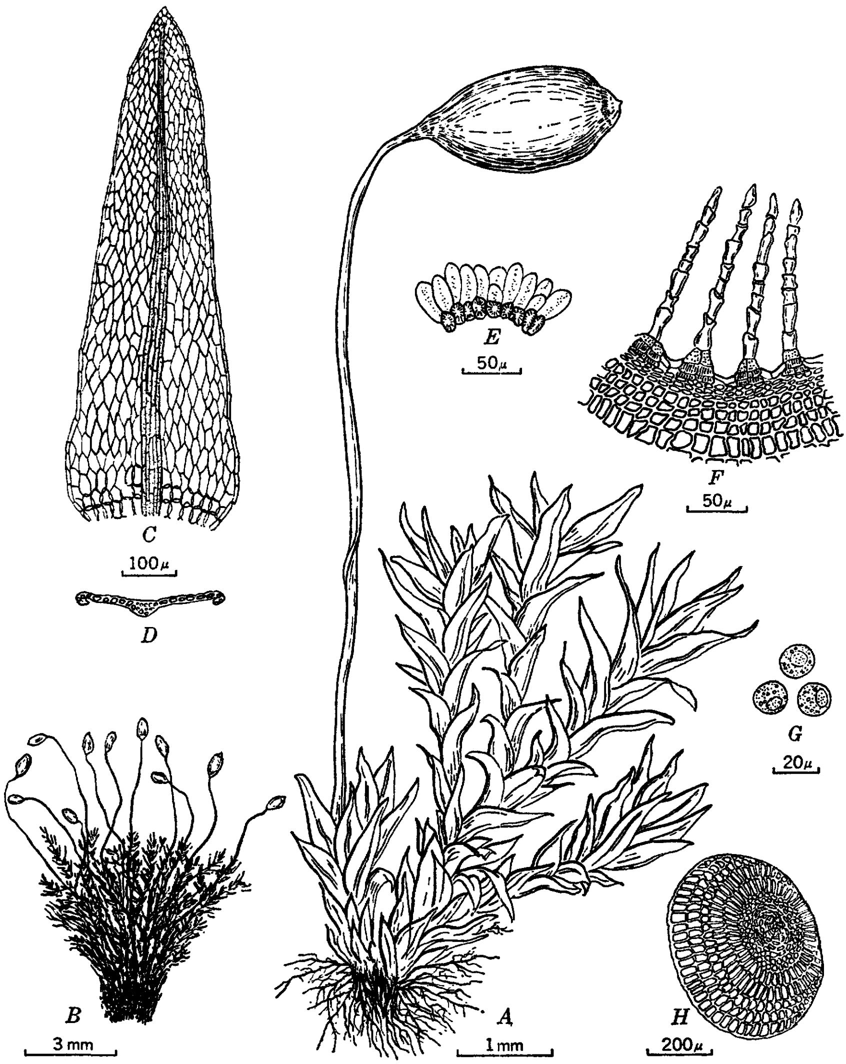

FIGURE 1.—*Mielichhoferia macrocarpa.* *A,* Female plant with mature capsule; *B,* sketch, showing habit of a tuft of fruiting plants; *C,* leaf from the middle of the stem; *D,* transverse section of the middle area of a leaf; *E,* a part of the annulus; *F,* a part of the peristome, showing 4 of the 16 teeth and exothecial cells; *G,* spores; *H,* operculum. Drawn from a moistened herbarium specimen (Shacklette 8181) from Amchitka Island, Alaska.

ACKNOWLEDGMENTS

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las, Tex., in collecting additional samples of the mosses and their substrates on Amchitka Island in April 1966. The drawings for this report were made by Mrs. Jessie M. Bowles. Mr. Melvin Johnson prepared the thin sections that were used to describe the rock samples.

REVIEW OF THE LITERATURE

The genus *Mielichhoferia* is one of several genera of copper mosses and is frequently discussed in the literature as containing many species that are found on sites of ore deposits or other metallic concentrations. Morton and Gams (1925), in their study of cave plants, reported many instances of the association of copper mosses (principally *Mielichhoferia elongata* Hornsch. and the closely related *M. nitida* Hornsch.) with mineral deposits. They wrote (p. 142 [translated]):

> The predilection of both species * * *, for copper-containing substrates has been known since their discovery [*M. nitida* in 1817] * * *. In addition to growing on copper ore—especially copper pyrite and its weathering products malachite and azurite—*Mielichhoferia* grows also on iron- and aluminum-rich silicate rocks.

These authors stated further (p. 143 [translated]):

> While there exists a great volume of literature on serpentine and calamine plants * * * there is at present very little known about the copper plants which include, besides *Mielichhoferia*, some liverworts. Apparently, there are no chemical and physiological researches on these bryophytes up to now; the rarity and exceptional difficulty of cultivation of these mosses makes research on them not easy to perform.

Mårtensson and Berggren (1954) analyzed substrates on which *Mielichhoferia elongata* and *Dryptodon atratus* (Mielichh.) Limpr. (*Grimmia atrata* Mielichh. ex Hornsch.) grew and reported 320–770 ppm (parts per million) copper. They wrote that these species—

> are resistant to (or perhaps may prefer) a substratum containing copper in amounts considerably higher (c. 100 times) than the trace concentration in ordinary soil. Further, the two mosses are able (or perhaps prefer) to grow on a substratum of exceptionally low pH. The question of the presence of other heavy metals in the substratum is still open.

Neither of these moss species occurs in North America. Persson (1956, p. 10) reported the copper in substrates of *M. elongata* in several northern European countries as follows:

> The Cu values vary between 30 and 450 ppm (in 5 times of 9 they are 150 or more) and on an average the value is 156; i.e., 5 times greater than for the "ordinary mosses."

Mårtensson (1956, p. 139–141) reported *Mielichhoferia elongata* from several localities in northern Swedish Lappland and found that four samples of the substrate of this moss contained from 50 to 159 ppm copper. In reporting other analyses of this moss he said:

> In no case have amounts of copper lower than 20 ppm been found in any sample. Moreover, the substratum is very acid * * *. Even if only a part of the total amount of copper in the substratum is present as soluble ions, their concentration cannot be very low at these low pH values. The acidity certainly depends greatly on the occurrence of sulphur (in pyrites or other minerals containing sulphur) * * *. The presence of other heavy metals in the substratum has not been investigated. The amount of [iron] is certainly very great.

He stated further that 5 ppm copper is generally accepted as the deficiency limit in ordinary soils and that amounts higher than 100 ppm are certainly poisonous for vascular plants where the substrate is not strongly basic.

In the southern Appalachian Mountains, *Mielichhoferia mielichhoferi* (Funck ex Hook.) Loeske (fig. 2) occurs on slaty rocks that are rich in pyrite (Schofield, 1959), and this moss has been discovered at a few other places in North America on rocks that have had some degree of mineralization; however, analyses of its substrates have not heretofore been published. *Mielichhoferia macrocarpa* is the only other species of this genus that is known to occur in North America north of Mexico. The distribution of this species was given by Andrews (1935, p. 186) as follows: "Disco Island of western Greenland, Arctic America, southward in Rocky Mts. to Colorado."

In contrast to the mineralized substrates of northern hemisphere species of *Mielichhoferia*, the few analyzed substrates of southern hemisphere species were reported to be not significantly mineralized. Persson (1956, p. 14) stated that the copper content of the substrates on which 14 species of this genus grew (mostly in the Andes Mountains of South America) was moderately low, averaging 28.7 ppm. He did not give the content of other metals in the substrates. Morton and Gams (1925, p. 142) stated that in the Andes Mountains *Mielichhoferia* species have a predilection for copper ore, but they presented no analyses of substrates. Noguchi (1956, p. 255) wrote, "In Europe and [elsewhere] it is well known that *Mielichhoferia* spp. are found on soil containing such metallic substances as copper and iron. But the author has not found any of the genus from such areas in Japan." However, Ochi (1959, p. 7) stated that analyses of substrates of *Mielichhoferia* had not been made in Japan.

The copper mosses are considered by some investigators to be more properly termed "sulfur mosses" because of their frequent association with sulfur compounds of copper, lead, zinc, and iron, as well as with sulfur deposits at mineral springs (Schatz, 1955, p. 115–117). However, these occurrences alone do not reveal whether the metal or the sulfur is the essential factor for the physiological processes of these

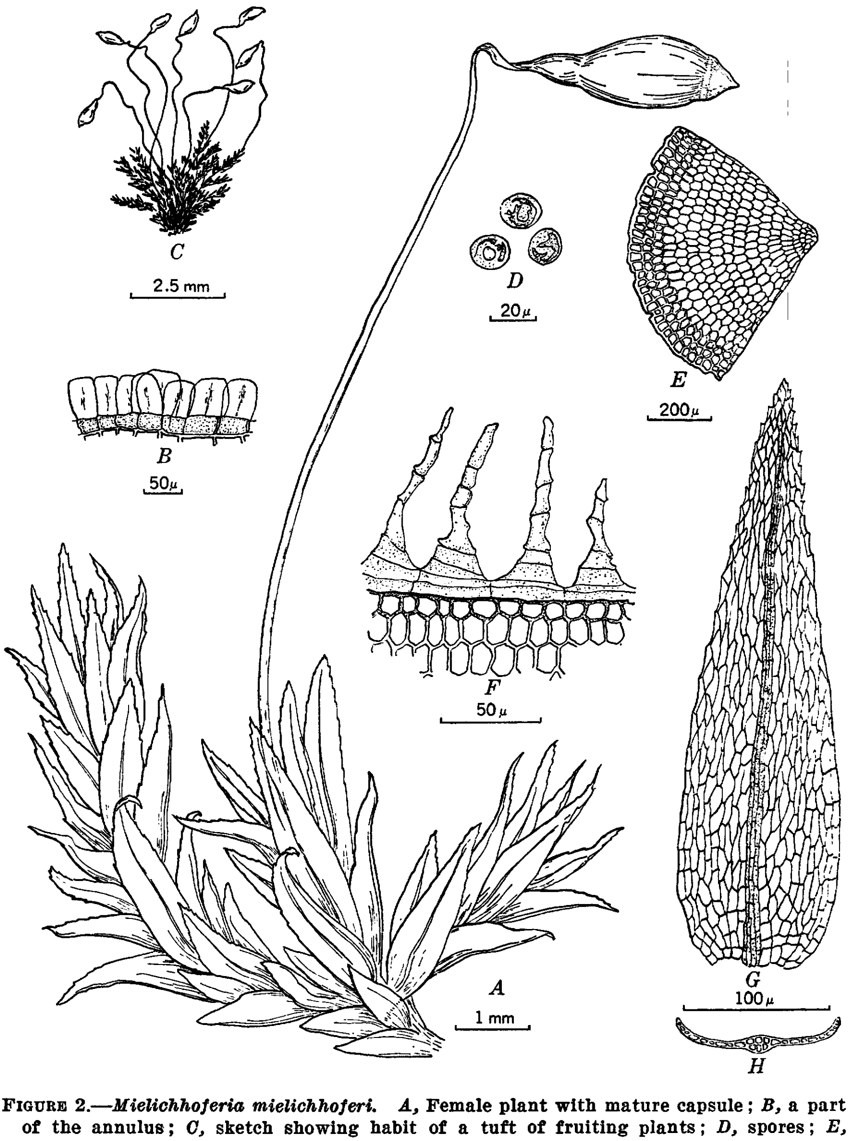

FIGURE 2.—*Mielichhoferia mielichhoferi.* *A,* Female plant with mature capsule; *B,* a part of the annulus; *C,* sketch showing habit of a tuft of fruiting plants; *D,* spores; *E,* operculum; *F,* a part of the peristome, showing 4 of the 16 teeth and exothecial cells; *G,* leaf from the middle of the stem; *H,* transverse section of the middle area of a leaf. Drawn from a moistened herbarium specimen (Shacklette 1999) from Alger County, Mich.

mosses or for the elimination of other plants that are competing for occupancy of a site. There seem to be no published analyses of the sulfur deposits on which these mosses grow; therefore it is not known if the deposits contain large amounts of heavy metals such as characterize the deposits at some springs. Conversely, it is not known if significant amounts of sulfur are present in some habitats of these mosses where the substrate is greatly enriched in a heavy metal that is not combined with sulfur. An example of this type of habitat is given by Noguchi (1956, p. 246, 250, and 252) in his report of the copper mosses *Merceya ligulata* (Spruce) Schimp. and *M. gedeana* (Lac.) Noguchi on stones of drains from copper roofs. This substrate most likely contains sulfur only in trace amounts; under ordinary atmospheric conditions the copper of a roof weathers to form only copper oxides or copper carbonates—not sulfur compounds of copper.

In summary, the published evidence of the association of *Mielichhoferia* species with concentrations of copper and other metals often is inconclusive, or even contradictory. Perhaps the explanation for these differing reports is that the tendency of these mosses to grow on mineralized substrates is a species characteristic, not a generic one, and that many of these reports have dealt with different species or biotypes. Some species may be obligate cuprophiles, whereas other species may be only facultative cuprophiles. Apparently many of the substrate evaluations that have been published were entirely subjective and were not supported by chemical analyses. Many more analyses of *Mielichhoferia* species and their substrates are needed to establish actual ecological relationships and to determine if any species of this genus can be named a "universal indicator," as this term is used by Nesvetaylova (1955) and Cannon (1960), of sites of metallic enrichment.

The genus *Merceya* contains only six species (Persson, 1948, p. 76), and all these probably are copper mosses. The relationship of some of these species to metals in the substrate was pointed out by Morton and Gams (1925, p. 41, 143) and confirmed by Persson (1948, p. 76) and Noguchi (1956). The distribution of *M. ligulata* (Spr.) Schimp. was described by Noguchi (1956, p. 239) as follows: "from Europe, through the Himalayas, Java, Japan, and North America to South America. It is a remarkable fact that *M. ligulata* grows only on soil containing such metallic substances as copper, iron, silver, etc., or on soil moistened with sulphuric water in hot springs areas." Persson (1956, p. 12) reported an average copper content of 94.5 ppm in the substrates of 11 samples of this moss that came from Java, India, Turkey, U.S.S.R., France, and Switzerland.

Merceya ligulata (reported by a synonym, *Scopelophila ligulata* Spruce) was first found in 1924 in North America by E. B. Bartram (1924) in Flux Canyon, Santa Cruz County, Ariz.; however, there appear to be no published chemical analyses of its substrate. This species was found by A. J. Sharp (1939, p. 292) in 1934 at Alum Cave, Sevier County, Tenn.; this location was described by Baur and Fulford (1934, p. 55) as a Civil War mining site. A third North American collection of this species was made by D. Richards, F. Drouett, and W. A. Lockhart in 1939 in a canyon 26 miles southwest of Cumpas, Sonora, Mexico (Bartram and Richards, 1941, p. 61). Persson (1956, p. 13) reported that the substrate of this specimen had a pH of 4.04 and a copper content of 110 ppm; he also noted that the identity of this specimen was questionable.

The occurrences of *Merceya ligulata* in Japan are of interest because of the variety of minerals on which the moss has been found. Noguchi (1956, p. 253) reported 15 collections of this moss that were associated with limonite, 1 with pyrrhotite, 3 with pyrite, 1 with copper, 1 with antimony, 1 "on rocks moistened by water running down from the gallery of a mine," and 1 on roadside rocks. In addition, the moss was found at two locations on rocks that were moistened by sulfurous water.

The only other species of *Merceya* that occurs in North America, *M. latifolia* Kindb. ex. Mac., was first collected by J. Macoun (Noguchi, 1956, p. 247) in 1887 on Vancouver Island, British Columbia. It was found again by R. S. Williams in 1899 at Great Falls, Mont., and the analyses of the substrate of William's collection was reported by Persson (1956, p. 13), who wrote, "Here a high Cu value, namely 320 ppm, is correlated with a very high pH value of 7.63. This is the highest [pH] value obtained among all the analyses presented here * * *. This is the only case where I have found a high Cu value combined with a high pH value." This species has been found only in western North America, and although it is not common, the following reports of it have been given: Utah, 7 locations (Flowers, 1936, p. 101); South Dakota, 1 location (Lawton, 1953, p. 118); Arizona, 1 location (McCleary, 1953, p. 125); and California, 1 location (Koch and Ikenberry, 1954, p. 292, 294), although other locations are known in this State. Except in the Montana location, nothing is known of the chemical nature of the substrates at the locations in the States listed above.

Certain species of leafy liverworts are reputed to grow only, or mostly, on substrates that are enriched in metals. At least one species, *Gymnocolea acutiloba* (Kaal.) K.M. appears to have value as an indicator of copper-enriched substrates, as was suggested by Morton and Gams (1925, p. 136), Reynaud-Beauverie (1936, p. 165), Müller (1951, p. 280–281), Schatz (1955, p. 113), and others. While I was collecting a large number of bryophytes in Alaska (see Persson, 1963), I found this liverwort at only two locations, both of which had a great enrichment of copper in their substrates (Shacklette, 1961, p. 4–5; 1965a, p. C4). Persson (1948, p. 77) said that *Gymnocolea acutiloba* is only one modification among many of *G. inflata* (Huds.) Dum. Because the taxonomic relationship of these two plants is not clear in the literature, the North American range of *G. acutiloba* (the plant with acute leaf segments) cannot be given accurately. The range of *G. inflata* was said by Frye and Clark (1944, p. 369) to extend from Greenland across the northern United States and southern Canada to Alaska. This species, listed by the synonym *Lophozia inflata* (Huds.) M. A. Howe, was found at Pictured Rocks, Alger County, Mich. (Nichols, 1933, p. 70); at the same location I collected the *Mielichhoferia mielichhoferi* substrate for which the chemical analyses are given in table 2 of this report.

Other liverwort species may have great tolerance for concentrated metals in their substrates (Shacklette, 1961, 1965a) but also can grow on nonmineralized sites. These plants may be of value as local indicators of mineral deposits, as was *Cephalozia bicuspidata* (L.) Dum. on lead and zinc ores in southeastern Alaska (Shacklette, 1965a, p. C8–C9). More chemical analyses of the substrates of certain liverwort species are needed to determine their relation to mineral deposits.

RESULTS

Plant and substrate samples were analyzed by chemists of the U.S. Geological Survey laboratories in Denver, Colo. The preparation of the samples and the analytical methods that were used followed procedures given by Shacklette (1965b) and by Ward, Lakin, Canney, and others (1963). The analytical results are given in table 1.

The volcanic rock at the Amchitka Island site contained amounts of copper, lead, and vanadium greater than the average in mafic rocks (Hawkes and Webb, 1962, p. 359–377). These amounts are much greater than the average values that are given for all igneous rocks. The contents of manganese, nickel, and zinc were significantly less than the average contents of mafic rocks. The amounts of elements in the two rock samples that are reported in table 1 generally are similar; however, the rock supporting *Mielichhoferia* contained five times as much chromium and somewhat more iron, nickel, lead, titanium, vanadium, yttrium, and zirconium than did the rock on which *Platydictya* grew, although the two samples occurred less than a meter apart.

The following descriptions of the two rock samples were prepared by W. R. Griffitts (written commun., May 1966) from his study of thin sections.

The two rocks differ primarily in texture and in degree of alteration, as both are composed mainly of labradorite feldspar, diopside or augite, and a little

TABLE 1.—*Chemical analyses of* Mielichhoferia macrocarpa *and* Platydictya jungermannioides *and their underlying rocks and soils, Amchitka Island, Alaska*

[Rock and soil analytical results given in percentage of dry weight; bryophytes analytical results given in percentage of ash. Laboratory number given in parentheses after genus. Nd, not detected; <, detected, but in amounts less than the stated value; >, greater than the stated value; ------, no data available. Analysts: David J. Grimes, J. C. Hamilton, Thelma G. Harms, Claude Huffman, Jr., J. D. Mensik, Wayne Mountjoy, Elwin L. Mosier, and L. F. Rader.]

Element or radical	Rock (volcanic) supporting—		Soil (lithosol) supporting—		Bryophytes		
	Mielichhoferia (D122422)	*Platydictya* (D122424)	*Mielichhoferia* (D122421)	*Platydictya* (D122423)	*Mielichhoferia* [1] (D411238)	*Platydictya* [2] (D411239)	Average amounts reported to be in bryophytes [3]
Ag	Nd	Nd	Nd	Nd	<0.0005	<0.0005	0.0009
Al	>5	>5	5	5	5	5	4.2
B	Nd	Nd	Nd	Nd	.07	.10	.0093
Ba	.02	.015	.01	.01	.02	.04	.4648
Be	Nd	Nd	Nd	Nd	Nd	Nd	.0006
Bi	<.002	<.002	Nd	Nd	Nd	Nd	.003
Ca	5.2	5.1	2.9	2.6	10	15	9.1
Co	.003	.003	.002	.0015	.002	.002	.0032
Cr	.015	.003	.003	.002	.001	.001	.0079
Cu	.015	.02	.02	.015	.1	.1	.0204
Fe	7	5	3	3	5	3	2.08
Ga	.002	.003	.0015	.0015	Nd	Nd	.0018
K	1.0	1.3	1.0	.75	2.1	------	4.2
La	Nd	Nd	Nd	Nd	Nd	Nd	.009
Mg	5	5	3	3	5	5	1.97
Mn	.07	.07	.07	.05	.2	.2	.3058
Mo	Nd	Nd	Nd	Nd	<.0004	<.0004	.0012
Nb	Nd	Nd	Nd	Nd	------	------	.005
Ni	.003	.002	.002	.002	.004	.004	.0083
P	.044	.03	.06	.09	1.2	1.5	.96
Pb	.003	.002	Nd	Nd	.002	.003	.186
Sc	.003	.003	.002	.0015	.0015	.001	.001
Sn	Nd	Nd	Nd	Nd	Nd	Nd	.002
SO_4	.01	<.01	.03	------	2.66	4.0	------
Sr	.07	.07	.05	.03	.1	.1	.0451
Ti	.5	.3	.2	.2	.2	.2	.196
V	.03	.02	.02	.015	.1	.1	.0071
Y	.003	.0015	.0015	.001	.002	.002	.005
Zn	.005	.0075	.005	.005	.1	.07	.152
Zr	.005	.003	.002	.002	.001	.001	.0124

[1] Ash is 15.4 percent of dry weight.
[2] Ash is 11.8 percent of dry weight.
[3] Average of samples described by Shacklette (1965b, p. D14); samples were not copper mosses and did not grow on mineralized substrates.

olivine and magnetite. Sample No. D411238 (the rock that supported *Mielichhoferia*) is a typical fine-grained basalt with many euhedral tablets that are about 0.02 mm thick and 0.14 mm long in parallel orientation, with a matrix of the other minerals. Sample No. D411239 (the rock that supported *Platydictya*) is a coarser, gabbroic rock, with subhedral feldspar crystals about 0.07×3.5 mm in size, without conspicuous alignment. Much of the pyroxene in this rock is partly altered to fine-grained pale actinolite. Round grains, now completely altered to actinolite and serpentine, may have been olivine. A little pyrite accompanies black opaque oxides in the actinolite masses.

The lithosols of the rock crevices show, in general, the same tendencies in element concentration as do the rocks. If the soils and rocks differ in the content of an element listed in table 1, the soils usually contain less of the element, a fact which indicates that in this environment the leaching of soils is very active and that plants are unable to enrich the soils by concentrating these elements that they obtain from bedrock. If the content of an element (except phosphorous) differs in the two soils, the soil that supports *Mielichhoferia* contains the greater amount.

The amounts of most elements in the soils, compared to the average amounts in soils as given by Hawkes and Webb (1962, p. 359–377), are nearly normal. However, the amount of copper in the soil of *Mielichhoferia* (200 ppm) is 10 times the average amount in soil and twice the extreme upper range in soils as given by these authors. The copper in the soil of *Platydictya* is one-fourth less than that in the soil of *Mielichhoferia.* The soils of both mosses have about two to three times the cobalt content of average soils, but have somewhat below average content of barium, chromium, and nickel. Perhaps these differences in concentration of elements in the substrates account for the patterns of occurrence of the two mosses and indicate that *Mielichhoferia* has considerably greater tolerance for concentrated metals than has *Platydictya.*

The element contents of the two moss samples that are reported in table 1 generally are similar; however, the amounts of ash that were obtained by burning the dry moss samples indicate that the *Mielichhoferia* sample contained about 30 percent contaminants (soil and rock) and the *Platydictya* sample, about 6 percent. Because of the dilution effect of these contaminants the *Mielichhoferia* sample must be judged to have had considerably greater amounts of the elements that are concentrated in mosses than the *Platydictya* sample had. Of the elements listed in this table, only chromium, iron, scandium, titanium, yttrium, and zirconium are more concentrated in the substrates than in the plant ash, but the differences in amounts are small.

In his report of a British copper moss Pigott (1958) wrote, "Attempts to discover whether copper is actively taken up by *Mielichhoferia* have been thwarted by the difficulty of obtaining adequate material which is absolutely clean of soil particles." Mårtensson and Berggren (1954) wrote concerning the same moss that they studied in Sweden, "We also tried to analyse the mosses, but it was not possible to free the tufts of alluvial sand, silt, and soil from the weathered schist." I have shown (Shacklette, 1965b, p. D17–D18) that for elements that ordinarily are concentrated in plants in amounts greater than occur in the substrate (copper is one of these elements) contamination of the sample by the substrate may not be a problem in demonstrating element uptake by bryophytes. If samples of both the substrate and the bryophyte are analyzed, the usefulness of the plant analysis can be evaluated. For example, for deposits having a copper content of 0.1 percent (1,000 ppm) or greater, contamination of the plant sample by the substrate may invalidate the results of plant analysis for this element. If the plant sample, however, contains more copper than is in the substrate, copper absorption by the plant is demonstrated. As a general guide, amounts of "ash" above 7–10 percent of the dry weight of the bryophyte sample should be considered to represent the amount of contamination of the sample.

If the amounts of elements in these mosses are compared to the average amounts in bryophytes that grew on nonmineralized substrates (Shacklette, 1965b, p. D14), significantly greater concentrations of certain elements in the two mosses are apparent. The most noteworthy concentrations are of copper, boron, and vanadium, which are about 5, 10, and 14 times, respectively, the average amount in bryophytes. The vanadium content of these mosses (0.1 percent) is probably the greatest that has been reported for any plant sample. Hawkes and Webb (1962, p. 377) gave the vanadium content of plant ash as 0.0022 percent, and I reported (Shacklette, 1965b, p. D14) 0.0023 percent as the average content in the ash of vascular plant samples. If allowances are made for the dilution factor of contaminants in the moss samples, the percentage of vanadium in the mosses is even greater than the reported value. The boron content is unusually great for mosses, and is about two to three times greater than the average of vascular plants. The Amchitka Island samples have, in addition, a greater than average content of some other elements, but the differences probably are not significant.

Data are not available for comparing the sulfur content of copper mosses to that of bryophytes in general; however, *Mielichhoferia macrocarpa* does not contain a large amount of sulfur if compared to cereals, and it contains probably less than one-third as much as is found in cabbage and related plants which are known to be accumulators of sulfur in large amounts (McMurtrey and Robinson, 1938, p. 826). The amount of sulfur in this copper moss is less than the amount in the *Platydictya* that grew near it, although the rock that supported *Mielichhoferia* contained more sulfur than did the other rock. The presence of pyrite in a thin section of the rock having the lower sulfur content and the absence of pyrite in a thin section of the rock having the higher sulfur content are contradictory; either the thin sections were not representative of the total rock samples, or the sulfur was combined with an element other than iron. The analyses in table 1 show that both mosses can concentrate sulfur in their tissues although they grew on rocks that had a low sulfur content.

The moss samples have less than average amounts of certain elements, and these differences appear to be significant for barium, lead, and zirconium. However, these elements are nonessential for plant growth; these low values would, therefore, have no effect on the plants.

In order to determine the element content of the substrates of some other copper mosses, I removed some of the soil from herbarium specimens that are in my collection and had it analyzed by emission spectrography and other methods. The samples are as follows: *Mielichhoferia mielichhoferi* that grew on Cambrian sandstone on the shore of Lake Superior at Pictured Rocks, Alger County, Mich., collected by me on July 5, 1941; *M. elongata* that grew on schist cobble on a lake shore, Pite lappmark County, Arjepluog Parish, North Swedish Lappland, collected by Gillis Een on Aug. 12, 1949; and *M. elongata* that grew on schist at the copper and silver mines of Sainte Marie au Fouilly, Département de la Haute Savoie, France, collector and date unknown. These samples were too small for chemical determinations of sulfur in the soils or for analyses to be made of the elements in the moss plants. The results of the substrate analyses are given in table 2. The discussion that follows compares the element content of these samples with the average element content of soils as given by Hawkes and Webb (1962, p. 359–377).

The substrate of *Mielichhoferia mielichhoferi* from Michigan contained 150 ppm copper, which is the same amount that was found in the rock that supported *M. macrocarpa* on Amchitka Island and which approximates the average copper value (156 ppm) of copper moss substrates in Europe, as was reported by Persson (1956, p. 10). This amount of copper is greater than 7 times the average amount in soils, and 3–15 times the amounts in sandstone. This substrate contained slightly more cobalt than the average amount in soils, and average or below average amounts of all other elements for which it was analyzed. If the presence of a concentration of heavy metal does determine the occurrence of this species at this site, copper must be the metal.

The substrate of *Mielichhoferia elongata* from Sweden contained only average or below average amounts of all elements that are listed in table 2. Although these results were not expected, particularly the low copper value of 10 ppm, they suggest an effect of sampling error. Great variation in a single sample of the substrate of this moss was experienced by Mårtensson (1956, p. 140), who wrote, "Further analyses * * * in which the amount of copper was determined polarographically indicate that the amount of copper, as expected, is discontinuous in the substratum. Thus four samples of one collection (Koublavagge) showed a copper content of 50.0, 70.4, 104 and 159 ppm." It should also be mentioned that the sample that I analyzed grew at an atypical site for this moss—on schist cobble of a lake shore. Ordinarily it is found in crevices of bedrock outcrops. However, this one occurrence of this species shows that it may be found on sites

TABLE 2.—*Chemical analyses of substrates, collected from Michigan, Sweden, and France, that supported* Mielichhoferia mielichhoferi *and* M. elongata

[Results given in percentage of dry weight; Nd, not detected; <, detected, but in amounts less than the stated value; sample number given in parentheses after location; analyst, Gary C. Curtin]

Element	Substrate supporting—		
	M. mielichhoferi	*M. elongata*	
	Michigan (HTS-109)	Sweden (HTS-110)	France (HTS-111)
Ag	Nd	Nd	0.0001
As	<0.02	<0.02	< .02
B	.001	.001	.002
Ba	.007	.05	.05
Be	.0002	.0002	.0001
Bi	<.001	<.001	<.001
Ca	.05	.2	.5
Cd	<.002	<.002	<.002
Co	.001	<.001	<.001
Cr	<.0005	.002	.001
Cu	.015	.001	.001
Fe	.1	2	1
Ga	<.001	.0015	.001
La	.003	<.002	.002
Mg	.05	1	.5
Mn	.01	.007	.005
Mo	<.0002	<.0002	.0002
Ni	.001	.0002	.0005
P	<.1	.15	.15
Pb	<.001	.001	.007
Sb	<.005	<.005	<.005
Sc	<.0005	.0005	.0005
Sn	<.001	<.001	<.001
Sr	<.005	.005	.005
Ti	.015	.3	.1
V	.001	.005	.003
W	<.005	<.005	<.005
Y	.0015	.001	.0015
Zn	<.02	<.02	<.02
Zr	.005	.02	.015

that are low in metal content, if the sample that was analyzed is assumed to be representative of its substrate at this location.

The soil from tufts of *Mielichhoferia elongata* from the silver and copper mines of France contained 10 times the amount of silver, 7 times the amount of lead, twice the amount of boron, and 1.2 times the amount of nickel that is found in average soils. The amounts of other elements were the same or less than the average amounts in soils.

SUMMARY AND CONCLUSIONS

Chemical analyses of the substrate of *Mielichhoferia macrocarpa* suggest that this plant is a copper moss and is a local indicator of mineral enrichment, as are other species of this genus. This study does not prove whether the plant's requirement for, or its tolerance of, certain concentrations of metals in the substrate determines its distribution. More studies of different occurrences of this species are necessary to establish it as a universal indicator.

The analysis of the substrate upon which *Mielichhoferia mielichhoferi* grew suggest that the plant also is an indicator of metal concentration in the substrate. The known range of this species is within eastern North America; this distribution complements the range of *M. macrocarpa* which has a western and northern distribution. The element contents of *Platydictya jungermannioides* and its substrates demonstrate that this moss has considerable tolerance to metals, as have many species of bryophytes, but that it is not adapted to highly mineralized substrates and therefore is not useful as an indicator species in mineral prospecting.

Reports in the literature indicate that species of the moss genus *Merceya* and the liverwort species *Gymnocolea acutiloba* commonly grow on substrates that are enriched in metals, particularly copper. Samples of these plants and their substrates were not available for this study, and there are no reports of analyses of them having been made for detecting metals other than copper.

Chemical analyses of the copper moss *Mielichhoferia macrocarpa* are presented for the first time. They show that this plant, when growing on a certain type of substrate, absorbs greater amounts of nutrient metals (boron, copper, iron, and magnesium) and vanadium, but lesser amounts of phytotoxic metals (chromium, nickel, and lead) than the average of other mosses that grew on nonmineralized substrates. However, the tendency in absorption is not necessarily advantageous to the plants because some of the nutrient elements are toxic to most plants if these elements are too greatly concentrated.

The presence of the copper moss on Amchitka Island does not appear to be determined by sulfur in the substrate. The amounts of sulfur in the substrates of the two moss species at this location are not large, and *Platydictya*, not the copper moss *Mielichhoferia*, contained the most sulfur yet it grew on rock that contained the least amount of sulfur. The question of whether the sulfur or the heavy metals in the substrate is the factor that influences the growth of these plants is of minor importance in considering the usefulness of the mosses as indicators of heavy metal concentrations. Substrates that have an enrichment in heavy metals commonly have also a concentration of sulfur that is greater than that of nonmineralized substrates.

The substrate of one of two samples of *Mielichhoferia elongata*, the most noteworthy copper moss in Europe, contained only average amounts of the elements, whereas the substrate of the other sample was greatly enriched in silver and lead and contained above average amounts of boron and nickel. However, both substrates contained less copper than the average amounts in soils and rocks (Hawkes and Webb, 1962, p. 364). This fact emphasizes the suggestion that the term "copper mosses" may be a misnomer for the mosses that appear to most commonly grow on a metal-rich substrate.

The tendencies of species in the genus *Mielichhoferia* to be regularly associated with greater than average amounts of heavy metals in their substrates should lead one to consider all occurrences of these plants as possible locations of useful deposits of minerals. However, a substrate may have lesser concentrations of heavy metals than constitute ore, yet provide sufficient amounts of these elements to adapt a site to the requirements of these mosses, as is shown by the analyses of the Amchitka Island rock and soil.

Ordinarily a search for copper mosses in the field is not practical as a prospecting method. These plants are very small (about 1 cm or less high), and the nonspecialist has difficulty in distinguishing them from many other bryophytes. In addition, other moss species can tolerate the metal content of many mineralized deposits but are not exclusively limited to such deposits—in Alaska 19 species of bryophytes have this characteristic (Shacklette, 1965a, p. C4–C6).

A practical method of using copper mosses in prospecting that has been used with success in locating copper deposits in Europe was described by Persson (1948, p. 78; 1956, p. 5). This procedure consists of examining the specimens of copper mosses that are preserved in the many university and government herbaria, noting the localities where the specimens grew, and examining the more promising localities by field reconnaissance and conventional prospecting methods. The more favorable sites may be further identified by chemical analysis of the small amounts of soil or rock that commonly cling to herbarium specimens of bryophytes. Of course, some of these localities already may be known to have mineral deposits or mines, and some may prove to have only slight enrichment of metals.

For prospecting in North America, I consider the mosses that are most useful as indicators of mineral deposits to be *Mielichhoferia macrocarpa*, *M. mielichhoferi*, *Merceya ligulata*, and *M. latifolia*. Some data suggest that the liverworts *Gymnocolea acutiloba* and *Cephalozia biscuspidata* may be useful local indicators of ore deposits, but their obligate relation to concentrations of metals has not been proven. One or another of these six species may be expected to be found in most of the United States and Canada, but insofar as is known all except *Cephalozia* are of rare and local occurrence only.

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