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Biogeochemical Characterization of an Undisturbed Highly Acidic, Metal-rich Bryophyte Habitat, East-Central Alaska, U.S.A.

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Abstract

We report on the geochemistry of soil and bryophyte-laden sediment and on the biogeochemistry of willows growing in an undisturbed volcanogenic massive sulfide deposit in the Alaska Range ecoregion of east-central Alaska. We also describe an unusual bryophyte assemblage found growing in the acidic metal-rich waters that drain the area. Ferricrete-cemented silty alluvial sediments within seeps and streams are covered with the liverwort *Gymnocolea inflata* whereas the mosses *Polytrichum commune* and *P. juniperinum* inhabit the area adjacent to the water and within the splash zone. Both the liverwort-encrusted sediment and *Polytrichum* thalli have high concentrations of major and trace metal cations (e.g., Al, As, Cu, Fe, Hg, La, Mn, Pb, and Zn). Soils in the area do not reflect the geochemical signature of the mineral deposit and we postulate they are influenced by the chemistry of eolian sediments derived from outside the deposit area. The willow, *Salix pulchra*, growing mostly within and adjacent to the larger streams, has much higher concentrations of Al, As, Cd, Cr, Fe, La, Pb, and Zn when compared to the same species collected in non-mineralized areas of Alaska. The Cd levels are especially high and are shown to exceed, by an order of magnitude, levels demonstrated to be toxic to ptarmigan in Colorado. Willow, growing in this naturally occurring metal-rich Red Mountain alteration zone, may adversely affect the health of browsing animals.

Introduction

In 2003, during geological and geochemical field studies in the Bonnifield mining district of east-central Alaska, various bryophytes (mosses and liverworts) were observed growing in and near acidic, metal-rich waters draining a large, undisturbed volcanogenic massive sulfide (VMS) mineral deposit. The area (Fig. 1), known as Red Mountain because of the various hues of red and orange in minerals within the alteration zone surrounding the mineral deposit, is alpine and located about 80 km south of Fairbanks near the northeastern flank of the Alaska Range. In June 2004, we revisited Red Mountain and investigated the occurrence and general ecology of the bryophytes that are growing in association with the deposit and to further characterize the biogeochemistry of selected woody plant species of the area.

Many terrestrial and aquatic bryophytes are known to accumulate large amounts of metals through direct ion exchange at the leaf surface and have been used in both mineral exploration studies (Shacklette, 1965; Brooks, 1983; Steinnes, 1995) and as biomonitors of airborne metal deposition (Berg and Steinnes, 1997). Some bryophytes are found most commonly on substrates high in particular metals (for example Cu or Pb) and may actually be restricted to this type of substrate (Shacklette, 1967; Shaw, 1987). Field studies of these occurrences are important from a phytogeographic, geobotanic, and ecophysiologic perspective (Cleavitt, 2005) and for understanding the habitat requirements of rare or unusual species. In this study we examine the geochemical characteristics of a mineralized area dominated by bioavailable forms of metals and metalloids and describe both the bryophyte assemblage that inhabits the area as well as the implications of high metal levels found in willow, an important component of the regional ecosystem, on the health of browsing animals.

Geological and Ecological Setting

The Bonnifield mining district is part of a loosely defined geographic area that is broadly mineralized and which extends in an arc from the Yukon Territory, Canada, through Alaska. This area is variously referred to as the Tintina Gold Belt (Goldfarb et al., 2000) or Tintina Gold Province (Hart et al., 2002). Because of the presence in the region of numerous VMS deposits, the Bonnifield mining district has long been a focus of mineral prospecting. Red Mountain, along with areas of the Yukon-Tanana Upland, about 150 km to the east, has recently been the target of intense renewed exploration activity in Alaska. Figure 1 is a map of the geology of the Red Mountain area.

The geology and mineral potential of the Bonnifield mining district and of Red Mountain are described by Wahrhaftig (1970), Gilbert (1977), Gilbert and Bundtzen (1979), Newberry et al. (1997), and Eppinger et al. (2004). The 26 VMS prospects in the district occur within a greenschist-facies assemblage of metavolcanic and metasedimentary rocks of the Yukon-Tanana terrane. Protolith rocks consist of felsic and mafic volcanic, subvolcanic intrusive, carbonaceous, and siliciclastic sedimentary rocks, indicative of a submarine, basinal setting (Wahrhaftig, 1970; Gilbert, 1977; Gilbert and Bundtzen, 1979). The volcanic rocks are Late Devonian to Early Mississippian (376–353 Ma) in age, compositionally bimodal, and emplaced in an extentional setting, inferred to be the attenuating continental margin of ancestral North America (Dusel-Bacon et al., 2004).

While actively explored through 1998, the Red Mountain deposit, which covers about 4 km^2, has never been mined. Mineralized rocks lie within the Mystic Creek member of the Totatlanika Schist (Fig. 1; Newberry et al., 1997; Smit, 1999). Red Mountain is a pyrite-rich VMS deposit containing sphalerite,

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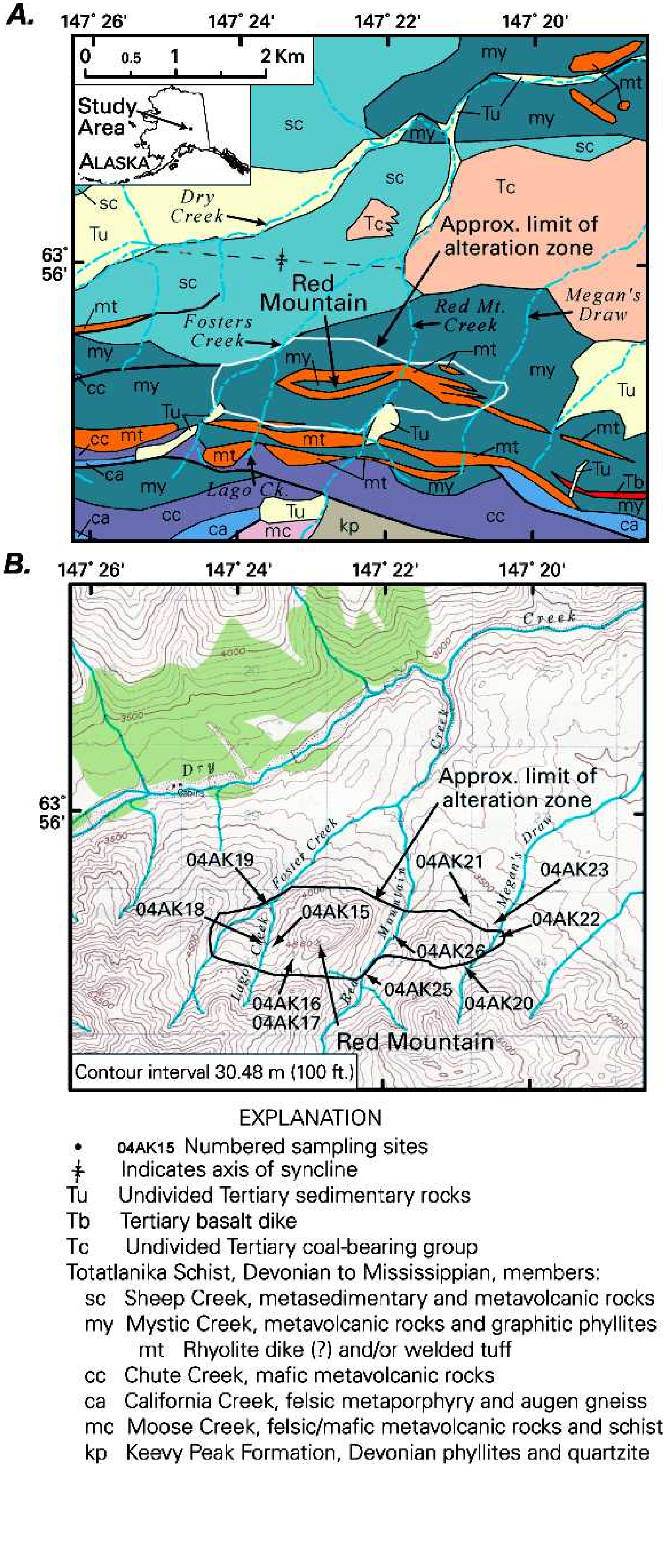

FIGURE 1. A. General geologic map of the area in and near the Red Mountain VMS deposit (after Gilbert [1977] and Eppinger et al. [2004]). B. Sampling site locations within and near the Red Mountain VMS deposit alteration zone (from USGS 1:63,360-scale Healy D-1 quadrangle map). Both figures are approximately the same scale and geographic extent.

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TABLE 1

Analytical methodology for plant, soil, and sediment material (Taggart, 2002; Crock et al., 1999).

Parameter	Method
Concentrations of Ag, Al, As, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Fe, Ga, K, La, Li, Mg, Mn, Mo, Na, Nb, Ni, P, Pb, Rb, Sb, Sc, Sr, Th, Ti, Tl, U, V, Y, Zn	ICP-MS[a]
Concentrations of Hg	CV-AAS[b]
Concentrations of total S	Combustion[c]
Concentrations of Se	HG-AAS[d]

[a] Inductively coupled plasma-mass spectrometry.
[b] Cold vapor-atomic absorption spectroscopy.
[c] Leco Sulfur Analyzer.
[d] Hydride generation-atomic absorption spectroscopy.

galena, chalcopyrite, and locally precious metals as outcropping and concealed massive to semimassive sulfides. Primary quartz-sericite-pyrite (QSP) footwall alteration is extensive and pyrite oxidation is prevalent.

Red Mountain lies in the Alaska Range foothills and is on the edge of the Alaska Range ecoregion (Nowacki et al., 2002; Fig. 1). The altitude of most of the Red Mountain area (800 m to 1800 m) is above the tree limit and alpine tundra shrubs, grasses, sedges, and forbs dominate the vegetation. Much of the steep slopes are scree and rubble whose stability is decreased by the rapid physical and chemical weathering of the extensive sulfidic alteration zone. Both permanent and intermittent streams, seeps, and springs permeate the slopes and ravines. In the mineralized areas, the submerged and emergent aquatic vegetation is dominated by bryophytes. Members of the forb and shrub genera *Ledum*, *Spirea*, *Cassiopie*, *Sedum*, *Empetrum*, *Vaccinium*, and others, dominate the drier areas between the seeps where there is a layer of soil. Here the extensive lichen, moss, and club moss cover consists of *Cetraria*, *Thamnolia*, *Cladina*, *Hylocomium*, *Bryum*, *Hypnum*, and *Lycopodium*.

Willow, grasses, and sedges dominate the riparian zone immediately beside the several permanent streams that drain both the mineralized and nonmineralized areas of Red Mountain. Feltleaf willow (*Salix alaxensis* (Anderss.) Cov.) and diamond-leaf willow (*S. pulchra* Cham.) are the most common colonizers of the gravely, saturated areas and benches within and near the streams.

As discussed by Eppinger et al. (2004), the Red Mountain deposit presents an ideal location to study acid generation, metal mobility and speciation, and the biogeochemical relation of plants to a metal deposit in a completely natural setting.

Methods

Figure 1 shows the areas that were sampled within and just downstream of the major QSP alteration zone. Field measurements of water from seeps, springs, and creeks, included pH, specific conductivity, alkalinity, acidity, dissolved oxygen, water temperature, Fe(II), turbidity, and a flow estimate. Representative water samples were collected at each site for further element analysis in the laboratory (for details on water sampling methodologies, protocols, and results, see Eppinger et al., 2004 and Eppinger et al., in press).

Iron-rich, cemented (ferricrete) sediment underlying the seeps and streams was sampled wherever water samples were collected and where aquatic bryophytes were observed. These samples consisted of the top-most 1 cm of sediment that also contained the liverwort *Gymnocolea inflata* (Huds.) Dum. We did not attempt to sample and analyze individual liverwort thalli. *Gymnocolea inflata* thalli are very small (commonly less than 1 mm), compact, and grow in intimate association with the silty Fe-rich sediments of the seeps and streams. As new sediment blankets the liverwort, the thalli grow upward resulting in a dense fibrous, ferricrete sediment below. We sampled the composite iron- and organic-rich sediment for chemical analysis. About 0.5 kg of composited sediment material was placed in paper USGS sampling bags for transport to the laboratory. In the laboratory, prior to analysis, the sediments were disaggregated and ground to pass an 80-mesh (0.177 mm particle size) sieve.

Samples of *Polytrichum commune* Hedw. and *P. juniperinum* Hedw. were collected at four sites for chemical analysis. These species were intermingled and the material sampled was a mixture of the stems, leaves, and rhyzoids of both. Samples were placed in paper USGS sampling bags and allowed to air dry. In the laboratory the samples were rinsed thoroughly with deionized, distilled water, dried in an oven at ambient temperature, ground in a Wiley Mill to pass a 2-mm screen, and ashed at 500°C.

Soil samples were collected near five of the bryophyte collection sites. The soils are poorly developed Gelisols that are dominated by silty colluvium. About 0.5 kg of a composite of the soil, mineral A1-horizon through C-horizon (channel sample), was collected and stored in paper USGS sampling bags. In the laboratory the soils were disaggregated and ground to pass an 80-mesh sieve.

At eight of the sites samples of the terminal 10–15 cm of diamondleaf willow stems (*Salix pulchra* Cham.) were collected and placed in Hubco™ polypropylene/cotton sampling bags. In the laboratory the material was rinsed thoroughly in deionized-distilled water, dried, ground in a Wiley Mill to pass a 2 mm screen, and ashed at 500°C.

Table 1 lists the laboratory methodologies used for the analysis of plant, soil, and stream sediment material. Details of the QA/QC protocols of the Denver laboratories of the US Geological Survey are given in Crock et al. (1999) and Taggart (2002). Duplicate samples were submitted at a rate of 10% of total samples. Data were accepted if recovery was $\pm15\%$ at five times the limit of detection and the relative standard deviation was $<15\%$ for the duplicate samples.

Results and Discussion

BRYOPHYTE ASSEMBLAGE

Figure 2 shows a typical bryophyte association found in acidic seeps and springs in the quartz-sericite-pyrite (QSP) alteration zone (Fig. 1). From a distance the stream/seep bryophyte-inhabited areas appeared black because of the visual dominance of *Gymnocolea inflata* (Huds.) Dum. Although this material contained a mixture of specimens that could be considered *Gymnocolea acutiloba* (or *G. inflata* subsp. *acutiloba*), we follow the taxonomic treatment of Grolle and Long (2000) and assign all of the material as *G. inflata*. At Red Mountain *G. inflata* occurred both in very damp sites (e.g., not in flowing water but on elevated microtopographic areas) and in areas with flowing water. In certain localities *G. inflata* would also appear dark green as well as black (Fig. 2).

Where present, *G. inflata* is associated with acidic habitats (so called "acid moors" as described by Arnell [1956], or "acid peats" as described by Watson [1968]). As confirmed by Eppinger

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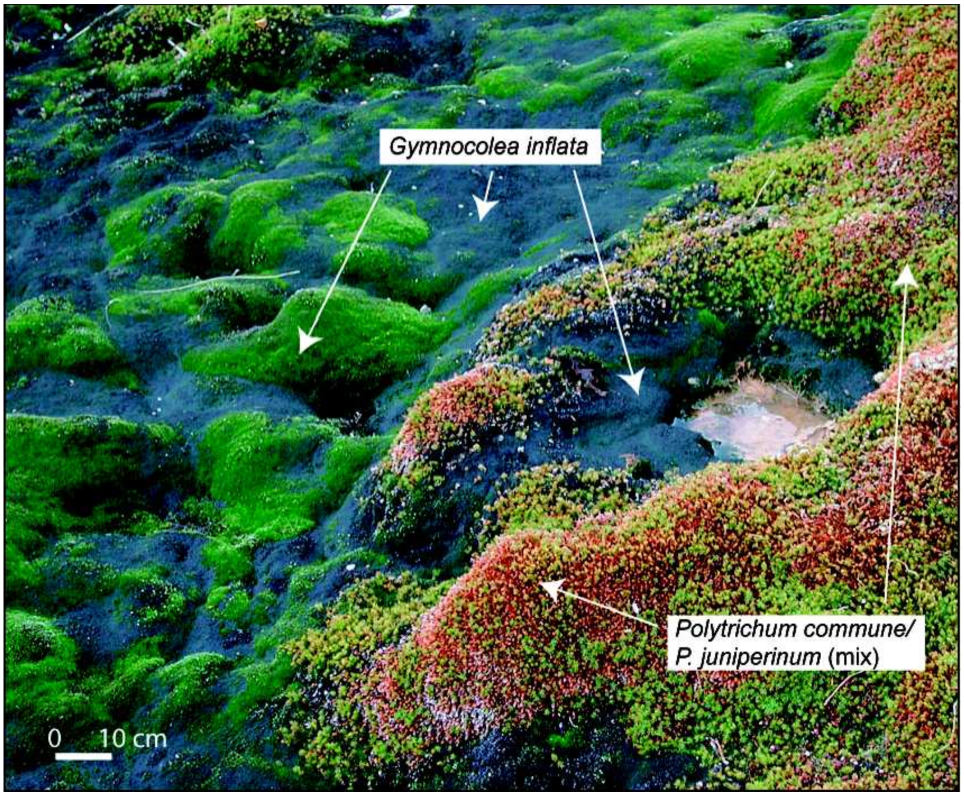

FIGURE 2. Moss species growing in areas influenced by acidic waters. *Gymnocolea inflata* (less damp areas are usually black and areas with flowing water, or that are very wet, are green), *Pohlia obtusifolia* (not shown), and polsters of *Polytrichum juniperinum* (reddish areas) mixed with *P. commune* (lacks a reddish appearance).

et al. (2004) at Red Mountain, cations and sulfate dominate the chemistry of acid waters draining sulfidic mineral deposits (Plumlee, 1999). It is unclear, however, whether the bryophytes in this assemblage are simply acidophilic or actually require an abundance of a particular heavy metal such as Cu (Shacklette, 1967). It has been a frequent observation that mosses of the genera *Mielichhoferia*, *Scopelophila*, *Dryptodon*, and *Crumia*, and a few liverworts, are most common on, if not completely restricted to, substrates enriched with heavy metals (Shaw, 1987).

Also found in association with *G. inflata*, but much less common, was the moss *Pohlia obtusifolia* (Brid.) L. Koch. Whereas *G. inflata* appeared green to black, *P. obtusifolia* was always a dull green color. *P. obtusifolia* is most commonly found

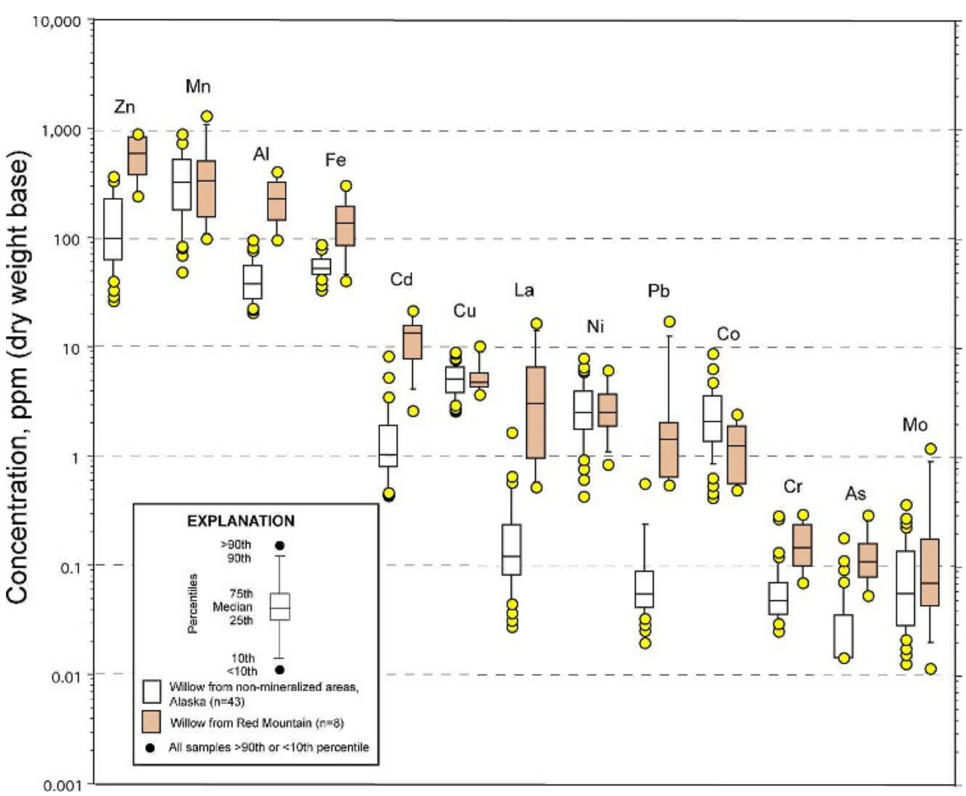

FIGURE 3. Concentration (ppm, dry weight basis) of trace elements in *Salix pulchra* collected at the Red Mountain VMS deposit compared to willow collected from various nonmineralized areas throughout Alaska.

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TABLE 2

Summary statistics for the concentration of elements in channel samples of Red Mountain soils and ferricrete sediment. Element mean concentrations for surficial materials from throughout Alaska are also presented for comparison. Concentrations are in parts per million (except as noted).

	Ferricrete Sediment (*n* = 6)		Composited Channel Soil sample (*n* = 5)		
Element	Range	Mean	Range	Mean	Surficial materials, Alaska (*n* is variable[a]; from Gough et al., 1988)
Ag	<3–5.3	nd	<3	nd[b]	nd
Al	32,300–86,800	63,000	66,400–72,100	69,300	65,000
As	10–75	46	16–27	21	9.6
Ba	590–1720	930	730–1180	990	678
Be	2.1–7.3	4.8	4.6–6.4	5.5	1.4
Bi	0.27–4.7	2.0	0.32–1.0	0.70	nd
Ca	340–1570	1070	780–1460	1180	20,000
Cd	0.11–1.4	0.5	0.06–1.5	0.53	nd
Ce	110–190	150	140–330	200	33
Co	1.2–3.3	2.4	2.8–12	6.6	14
Cr	9.0–22	14	12–30	22	64
Cs	1.2–3.7	2.4	2.0–2.8	2.6	nd
Cu	50–220	130	36–67	49	29
Fe	51,000–240,000	118,000	33,000–60,000	48,800	38,000
Ga	14–51	35	30–36	33	16
Hg	0.40–0.90	0.30	0.04–0.07	0.06	nd
K	14,600–41,800	29,300	29,700–32,800	31,800	13,000
La	49–95	73	73–180	100	21
Li	10–28	19	21–25	23	30
Mg	6050–18,100	11,100	10,700–21,400	14,800	12,000
Mn	134–560	270	270–1,040	600	670
Mo	3.4–23	15	4.6–9.8	7.4	1.3
Na	1470–6680	3890	3,610–4620	4370	15,000
Nb	55–180	120	120–180	150	9.0
Ni	2.5–6.9	4.5	6.0–8.8	7.2	33
P	260–620	400	430–560	500	860
Pb	480–3000	1130	130–284	210	14
Rb	68–200	140	140–160	150	nd
S	2900–21,000	9700	600–2200	1,520	nd
Sb	1.3–19	7.4	1.4–3.4	2.5	nd
Sc	3.0–12	5.8	8.2–14	10	14
Se	0.80–4.9	2.6	0.90–1.4	1.2	nd
Sr	16–27	23	13–30	23	198
Th	16–56	38	32–38	35	7.6
Ti	1100–3300	1,880	3200–4600	3600	5200
Tl	0.90–4.9	2.8	1.1–1.5	1.3	nd
U	4.1–13	8.9	8.3–9.7	8.9	2.8
V	52–160	76	95–120	105	129
Y	45–130	93	78–170	120	15
Zn	110–670	330	100–410	240	79
pH[c]	nd	nd	5.1–5.4	5.3	5.6

[a] The arithmetic mean was based on 78 to 437 samples, depending on the element.
[b] Not determined.
[c] Standard units.

in cold, wet areas (Nyholm, 1969; Demaret and Wilczek, 1980; Smith, 1982), for example in alpine and subalpine environments near the edge of snow fields; we could find to mention in the literature of its association with acidic waters.

Of particular interest was the appearance of a mix of the haircap mosses *Polytrichum commune* Hedw. and *P. juniperinum* Hedw. within the splash zone of the seeps and small streams (Fig. 2). At Red Mountain the acidic, metal-rich waters (Eppinger et al., 2004) are an important component of the *Polytrichum* habitat. When ice free, the water is introduced both through capillary upward movement and aerial spray deposition. The moss grows in polsters (small mounds) that are 10 to 20 cm high (Fig. 2) and occurs in luxuriant mixed populations when present near the seeps. Both of these species are initial colonizers of disturbed ground (Coxson and Marsh, 2001), such as a post-fire landscape. Glaser et al. (1990; 1997) report the presence of *Polytrichum strictum* and *P. juniperinum* growing on raised bogs in Minnesota where the pH of the surface water ranged from 3.8 to 4.2. We found no mention in the literature of *Polytrichum* being associated with highly acidic mineralized substrates or waters.

BRYOPHYTE SUBSTRATE GEOCHEMISTRY

Eppinger et al. (2004, in press) characterize the waters within the QSP alteration zone as sulfate dominant with high concentra-

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tions of Al, Cd, Co, Cu, Fe, Mn, Ni, Pb, Y, Zn, and the rare earth elements; and to a lesser extent F^- and Si. These authors found that concentrations of total dissolved solids mimic those of sulfate and were highest in the QSP alteration zone. Upstream of the alteration zone we found that all streams had pH values of 6.5 or greater and conductivities from 370 to 830 $\mu S\ cm^{-1}$, whereas within the QSP alteration zone, pH values below 3.5 (as low as 2.4) and conductivities above 2500 $\mu S\ cm^{-1}$ (up to 3400) were common. Stream sediments are anomalous in Zn, Pb, S, Fe, Cu, As, Co, Sb, and Cd relative to local and regional background values (Eppinger et al., in press). Within the portion of the QSP alteration zone where this bryophyte association was observed, the pH of the water in 2003 varied from 2.7 to 3.3 (with conductivities of 1270 to 3410 $\mu S\ cm^{-1}$) and in 2004 varied from 2.6 to 4.5 (with conductivities of 1350 to 4800 $\mu S\ cm^{-1}$).

The water within and immediately below the QSP alteration zone had extremely high concentrations of trace elements (Eppinger et al., 2004); for example: Zn (mean, 41,000 $\mu g\ L^{-1}$; median, 13,000 $\mu g\ L^{-1}$), Mn (mean, 8500 $\mu g\ L^{-1}$; median, 4200 $\mu g\ L^{-1}$), and the rare earth elements (mean, 6100 $\mu g\ L^{-1}$, median 3200 $\mu g\ L^{-1}$). Other metals having high concentrations and associated high means include Al, Fe, Cd, and Cu, and to a lesser extent Co, Ni, and Pb.

Summary statistics for analyses of the sampled sediment (including ferricrete, silty alluvium, and liverwort thalli) are reported in Table 2. Compared to both the Red Mountain soils and surficial materials from throughout Alaska (Table 2), the Red Mountain iron-rich sediment samples showed notably higher concentrations of As, Cu, Fe, Hg, La, Pb, S, and Sb. Concentrations of Cd in surficial materials were not reported for Alaska in Gough et al. (1988); however, when compared to soils collected since 1988 by the authors (Gough et al., 2001; 2005), the Cd levels in the Red Mountain material were not unusual (Red Mountain: mean, 0.53 ppm in soil, 0.50 ppm in sediment; nonmineralized areas of Alaska: mean, 0.30 ppm). Concentrations of other elements in sediment associated with VMS deposits (Co, Cr, Mn, Ni, and Zn) either differed little from amounts found in Red Mountain soils and Alaska surficial materials or contained somewhat less.

WILLOW BIOGEOCHEMISTRY

We compare the concentration ranges of 13 trace elements in willow leaves from 8 samples of *S. pulchra* collected at Red Mountain with similar material collected from nonmineralized areas in Alaska (Fig. 3). The 43 samples from the nonmineralized areas are a mixture of *S. pulchra* and *S. glauca*. These species are combined here because we are unsure about the exact taxonomic validity of these collections (the two species are very similar in physiognomy and habitat). Past studies have shown that the trace element concentration of these two species, when growing in areas with identical soils, is similar (Gough et al., 2001). The values in Figure 4 are expressed as percentiles in a box-plot format. The concentrations are in parts per million, dry weight basis, and the elements are arbitrarily arranged from highest to lowest median concentration.

Most of the elements (Al, As, Cd, Cr, Fe, La, Pb, and Zn) showed large differences (over an order of magnitude for Cd, La, and Pb) between the median values of the two willow populations with higher concentrations in willows from the mineralized area. The mobility and bioavailability of the metal cations is enhanced by the low soil (Table 2) and water pH values (Eppinger et al., 2004); however, the absolute amounts of the metal cations in Red Mountain soils, compared to values for soils from throughout the state of Alaska, are very similar (Table 2). These soils, therefore, do not reflect a geochemical signature expected of the mineral deposit and are either readily leached, are composed of non-mineralized colluvium, or are influenced by eolian sediments derived from outside the deposit area. Because these soils have a silty texture throughout their profile, we postulate that they are eolian derived. Eolian material, most likely Holocene in age, is common in this part of interior Alaska because of numerous source regions (Muhs, et al., 2003).

The bioavailability of As and Mo, elements that occur commonly as oxyanions in soils, should be retarded by the low soil pH values (Kabata-Pendias and Pendias, 2001), yet their concentration in the Red Mountain willows is greater (Fig. 3) than the concentration in the willows from the nonmineralized areas. We did not determine the phase association of these trace elements within the soil, however, the total concentration of As and Mo in Red Mountain soil is greater than the state-wide soil average (Table 2) and these higher total levels, depending on their form, could be an important factor in the enhanced uptake of these elements by willow.

The chemistry of Red Mountain willows is of concern because willows are an important food source for a number of mammals and birds (for example, browsing moose, hare, and ptarmigan). Willow is also known to bioaccumulate Cd (Gough et al., 2001). The concentrations of Cd (mean, 13 ppm; median, 12 ppm) and Pb (mean, 3.2 ppm; median, 1.4 ppm) in Red Mountain willow are especially interesting because these concentrations are an order of magnitude greater than those found in willow leaves from nonmineralized areas. Larison et al. (2000) reported that Cd concentrations of about 2.2 ppm or greater in willow leaf buds inhibited proper renal development of ptarmigan in Colorado. Despite the limited geographic extent of the mineralized zone, the potential may exist for an adverse impact on the health of browsing animals (Gough et al., 2002). Most Pb in soil is unavailable for uptake (Kabata-Pendias and Pendias, 2001); however, in soils with low pH and low amounts of organic matter, Pb is mobile. Although anomalous for willow, these Pb levels are not particularly high for vegetation growing in contaminated environments (Kabata-Pendias and Pendias, 2001).

ELEMENT CONCENTRATIONS IN POLYTRICHUM

Concentrations of elements in the dry material of four samples of *Polytrichum commune/P. juniperinum* mix are reported in Table 3. Also listed for comparison are data for another terrestrial moss, *Hylocomium splendens* (Hedw.) DSG, collected in an unmineralized area of the Kenai Peninsula of Alaska (Severson et al., 1990). Although these two species have different growth habits, both are often found together in high latitude alpine and subalpine areas. We do not know how similar their inorganic chemistries would be if collected contiguously, but the concentration of some of the major elements in these two populations are quite similar (Mg, K, and P as well as ash yield). Maritime climatic influences and carbonate-rich soils associated with the *Hylocomium* collections may explain the dissimilarity in the major elements Na and Ca, respectively. The trace element and metal cation levels in *Polytrichum* from Red Mountain are considerably higher than the levels in *Hylocomium* (As, Cu, Fe, Hg, Mn, Pb, Zn, and the rare earth elements La, Ce, as well as Y). We assume that this difference is the direct result of element uptake from the large dissolved metal load in the water that bathes

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TABLE 3

Average and range for the concentration of elements in *Polytrichum commune/juniperinum* mix (this study) and *Hylocomium splendens* (Severson et al., 1990). Concentrations are in parts per million, dry weight basis (except as noted).

Element	*Polytricum* Arithmetic mean ($n = 4$)	*Hylocomium* Geometric mean ($n = 21$)
Ash yield[a]	7.5	7.5
Ag	4.4	nd[b]
Al	7870	3740
As	2.3	0.14
Ba	93	69
Be	0.59	nd
Bi	0.08	nd
Ca	2200	6830
Cd	2.2	nd
Ce	210	1.3
Co	2.1	1.1
Cr	2.4	3.4
Cs	0.27	nd
Cu	290	4.6
Fe	6170	1740
Ga	2.6	0.9
Hg	0.25	0.09
K	4560	4200
La	75	1.2
Li	2.1	0.9
Mg	1590	1620
Mn	130	450
Mo	0.77	nd
Na	320	1320
Nb	5.5	nd
Ni	2.9	2.0
P	920	1200
Pb	120	2.1
Rb	27	nd
S	nd	720
Sb	0.4	nd
Sc	1.1	0.60
Se	0.26	0.06
Sr	8.6	44
Th	2.8	nd
Ti	120	170
Tl	0.17	nd
U	5.5	nd
V	6.2	5.3
Y	20	0.94
Zn	570	34

[a] Percent.
[b] Not determined.

the moss and of the bioavailable forms of these metals in the sediment.

Conclusions

The Red Mountain quartz-sericite-pyrite (QSP) alteration zone, and the VMS deposit that it is part of, are characterized as having acidic (as low as pH 2.4) metal-rich, high sulfate waters, active ferricrete formation in the silty alluvial sediments, and an abundance of primary (pyrite) and secondary (sulfate) acid-generating minerals. The seeps, springs, and streams that are found within the QSP alteration zone, or that are outside of the zone but influenced by the acid groundwaters within the zone, are inhabited by an unusual bryophyte community dominated by the liverwort *Gymnocolia inflata* in the areas with standing or flowing water and the mosses *Polytrichum commune* and *P. juniperinum* adjacent to, but elevated above, the water. Both the sediment upon which the liverwort grows and the *Polytrichum* thalli that receive acidic metal-laden spray have high concentrations of some major and trace metals, especially As, Cd, Cu, Fe, Hg, Pb, and Zn. We do not speculate as to whether *G. inflata* is acidophilic or actually may require high concentrations of a dissolved metal, such as Cu. It is curious, however, that *P. commune–P. juniperinum* dominate the vegetation of the splash zone near the acidic metal-rich waters when we could find no report in the literature of similar observations.

The shallow Gelisols that are found throughout the QSP alteration zone are, in general, similar in their major and trace element chemistry to soils found throughout Alaska. However, the willows that grow in the areas next to the flowing water and that have their root systems more in the sediment than in the soil have much higher major and trace element levels than the same willow species growing in non-mineralized areas of Alaska (especially Al, As, Cd, Cr, Fe, La, and Pb, Fig. 3). The concentrations of Cd in willow from Red Mountain are an order of magnitude above levels found to be toxic to ptarmigan in the Colorado Mineral district. It would be interesting to investigate the possible toxicity to local species that depend on willow for winter browse (i.e., ptarmigan, moose, and hare).

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