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ANALYSIS OF ROCKY MOUNTAIN LICHENS USING PIXE: CHARACTERISTICS OF IRON AND TITANIUM

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Lichens have been shown to be effective biomonitors of air quality. They are currently being used to characterize background element levels and to identify air pollution effects on federally administered lands in the Rocky Mountain region of the western United States. PIXE analysis for twenty elements has been performed on over two hundred lichen specimens collected from various national forests, national monuments, and national parks in the region. This paper reports on patterns of iron and titanium accumulation in lichen tissues. Data show a strong relationship between concentrations of iron and titanium. The Fe/Ti ratios agree well with values reported in similar lichen studies; however, our values for both iron and titanium concentrations are ten times greater than other reports. A distribution function for the log of iron concentrations is distinctly bimodal. The lower concentration mode contains fruticose lichens from bark substrates and the higher concentration mode contains foliose lichens from rock substrates. High iron concentrations in fruticose lichens along the Wasatch Front suggest air pollution impact from a local steel plant.

INTRODUCTION

Over the last several decades lichens have been used extensively as biomonitors of air quality (1). Lichens are non-vascular, composite organisms consisting of a fungus and an alga or cyanobacterium which live together in a complex symbiotic relationship. Lichens, which lack a true root system, obtain most of their nutrients through wet and dry atmospheric deposition. Lichens demonstrate several growth form patterns. In this study species of the foliose and fruticose growth forms were used. Foliose lichens are dorsoventrally flattened and generally somewhat adherent to the substrate. Foliose species commonly occur on either rock or bark. Fruticose species are densely branched with a single point of attachment and generally occur on bark. Due to differences in attachment patterns, foliose species have a greater degree of contact with the substrate.

In the last fifteen years we have established lichen air quality biomonitoring baselines throughout the Intermountain Area. Most of our work has been in federally administered wilderness areas and national parks and monuments. One interesting observation from our work has been the relationship between iron and titanium concentrations in lichen thalli. Other researchers, particularly Takala, *et al.* (2) and Nieboer, *et al.*(3), have also reported on iron and titanium concentrations in lichens. While these other studies used different analytical methods, their data is comparable to ours. Nieboer, *et al.*(4) have suggested that due to the relative consistency of iron/titanium ratios it should be possible to accurately predict accumulation of iron or titanium by lichens from air pollution sources.

EXPERIMENTAL

A total of 204 lichens from fourteen sites in Idaho, Utah, Montana, Wyoming, Colorado, and Arizona were sampled. Approximately 70% of the specimens were from the following list: *Letharia vulpina* (22%), *Xanthoparmelia cumberlandia* (19%), *Rhizoplaca melanophthalma* (10%), *Usnea hirta* (9%), *Umbilicaria vellea*(6%), and *Xanthoria polycarpa*(5%). Due to unique species distribution patterns, not all species were present at each site. Lichen samples were detached from the substrate, transported to Brigham Young University, and prepared as described by Williams, *et al.*(5). A minor deviation from this procedure was used for small samples. Cutting up the sample in a blender

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TABLE 1. Average Fe/Ti ratio for each site with standard deviation and number of lichens sampled.

Site[a]	Mean Fe/Ti	s	Fe range (ppm)	N	Site	Mean Fe/Ti	s	Fe range (ppm)	N
Salmon N. F.	7.55	2.0	47.8-6880	53	High Uinta W. A.	6.61	.85	1050-4000	7
Sawtooth N. F.	8.30	3.1	190-2200	6	Clearwater N. F.	8.08	2.0	83.5-7440	10
Manti-Lasal N. F.	8.14	1.1	1950-4570	6	Nez Perce N. F.	6.25	1.3	90-3310	8
Cedar Breaks N. M.	6.78	.93	2400-7900	4	Fort Bowie N. H. S.	6.89	.45	7190-26000	2
Anaconda-Pintler W. A.	6.10	1.6	170-8700	17	Uinta N. F.	9.51	1.4	1570-16800	22
Capitol Reef N. P.	6.15	1.5	3860-5740	3	San Juan N. F.	7.26	1.1	292-13100	39
Bridger-Teton W. A.	7.62	1.8	500-8600	7	Chiricahua N. M.	7.77	.74	95.8-11700	19

[a]Abbreviations: N. F. (National Forest), N. M. (National Monument), N. P. (National Park), W. A. (Wilderness Area), N.H.S. (National Historic Site).

was deemed unnecessary. Instead, the sample was placed directly into a teflon vessel, and homogenized in a Mikro-Dismembrator. Approximately 1 milligram of powdered lichen sample was secured to a thin polycarbonate film with polystyrene dissolved in toluene. Samples approximately 1 mg/cm^2 thick were then irradiated with a beam of 2.25 MeV protons. Data analysis procedures are also described in Williams, *et al.*(5).

DISCUSSION

The Fe/Ti ratio for a set of samples was calculated as

$$Fe/Ti = \sum(Fe/Ti)_i/N$$

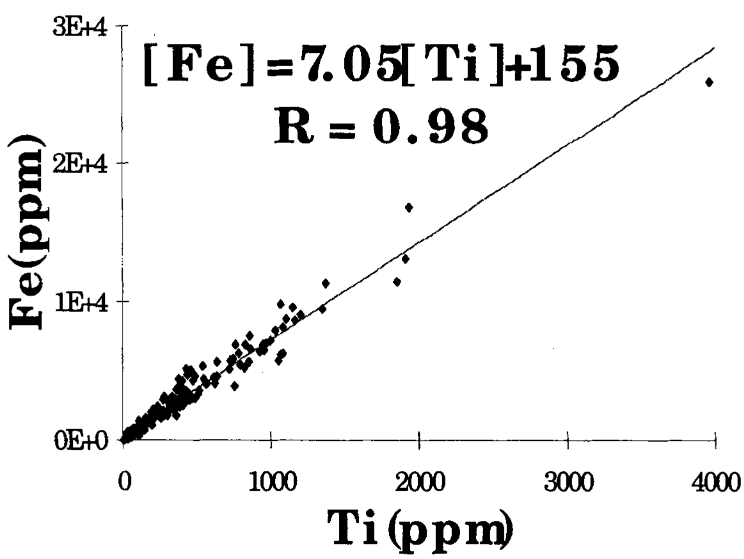

Figure 1. Iron concentration versus titanium concentration for 204 lichens.

where $(Fe/Ti)_i$ is the ratio for a single sample in the set and N is the number of samples. Figure 1 plots iron concentration versus titanium concentration for all 204 lichens along with a linear regression line through the data. The equation for the line and the R value are also given. The correlation is remarkably strong, even at higher concentrations. This is because iron and titanium oxides are thought to form under similar geological conditions. The slope of 7.05 is quite consistent with the average lithosphere ratio of Fe/Ti = 6.5 (6). A similar study in New Brunswick, Canada by Nieboer, *et al.*(3) reported Fe/Ti ratios for *Cladonia* spp. of 8.6 with an iron range from 242 to 1292 ppm. A study in Finland by Takala *et al.*(2) report Fe/Ti ratios of 7.46 and 6.12 for *Hypogymnia physodes* and *Pseudevernia furfuracea* with iron ranges of 450 to 2580 and 700 to 1720 ppm respectively. The iron range for our study was 47.8 to 26,000 ppm. The ratios in these studies are consistent with ratios in this study; however, both studies cite ranges for Fe and Ti which are more than an order of magnitude less than our samples.

The mean Fe/Ti ratios for this study were calculated for each site (Table 1). Some variance between sites is expected, but most ratios fall between 6 and 8.5. One exception is the samples from the Uinta National Forest. This forest includes much of the of the Wasatch Mountains (commonly known as the Wasatch Front) which extend in part from the north to the south end of Utah Valley, a distance of approximately 50 miles. The Fe/Ti ratio from this area (9.51) is the highest of any of our sites in the Rocky Mountains. If this site is set aside ratios for all other sites agree within their standard deviations.

TABLE 2. Average Fe/Ti ratio for 6 species.

Genus/Species	Mean Fe/Ti	s	N
Xanthoparmelia cumberlandia	7.35	0.90	39
Letharia vulpina	6.31	1.4	44
Rhizoplaca melanophthalma	7.20	1.2	21
Usnea hirta	7.67	1.1	18
Umbilicaria vellea	8.96	1.9	13
Xanthoria polycarpa	10.0	1.3	11

Fe/Ti ratios for the six most commonly sampled species are reported in Table 2. All agree within standard deviations except for *Xanthoria polycarpa*, which has a high value of 10.0. All samples for this species are from the Uinta National Forest and were collected along the Wasatch Front. The two most frequently collected lichens are *Letharia vulpina* (a fruticose lichen) and *Xanthoparmelia cumberlandia* (foliose lichen). *Letharia vulpina* was collected primarily in north central Idaho and Montana, while *Xanthoparmelia cumberlandia* was collected extensively from sites throughout the Intermountain area.

The average Fe/Ti ratio for foliose lichens was 7.81 with a standard deviation of 2.1 while fruticose lichens had a Fe/Ti ratio of 7.46 with standard deviation of 2.3. These data suggest that there is not a significant difference in Fe/Ti ratios for the two growth forms when averaged across all samples.

The distribution functions of the log of iron concentrations were plotted for fruticose and foliose lichens and is shown in Fig. 2. Instead of a single distribution, two separate peaks occur. These distributions patterns show that foliose lichens have much higher iron concentrations (10x) than fruticose lichens. Separation between the two distributions occurs at 1250 ppm iron. The mean and standard deviation of the data on the logarithmic scale for both iron and titanium are given in Table 3. One possible explanation for iron concentration differences between growth forms may be the fact that the foliose species (mostly *Xanthoparmelia cumberlandia*) used in this study occur exclusively on rock substrates; which may result in greater access to and uptake of soil and ultra-fine rock debris. As may be inferred from the strong correlation between iron and titanium, the titanium distribution follows a similar bimodal pattern.

TABLE 3. Log[Fe] and log[Ti] distribution data.

Growth Form	log [Fe] Mean	log [Fe] s	log [Ti] Mean	log [Ti] s
Fruticose	2.75	0.44	1.90	0.39
Foliose	3.50	0.33	2.62	0.35

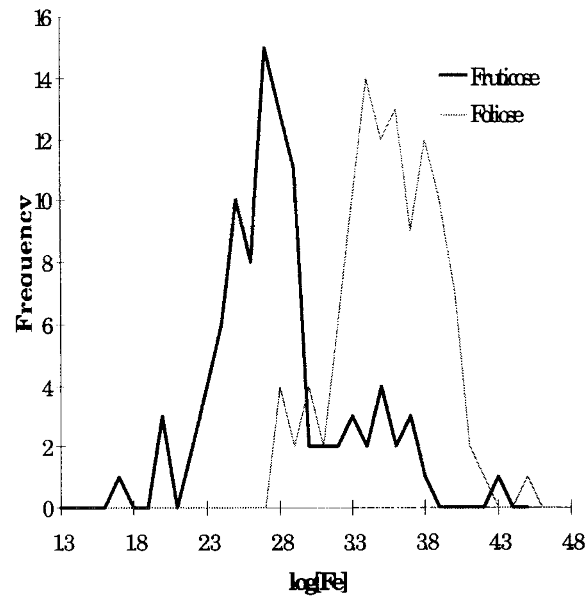

Figure 2. Log [Fe] distribution for fruticose and foliose lichens.

One area of particular interest occurs for 3.2<log[Fe]<3.7. The fruticose distribution follows a descending trend between 2.7 and 3.2, but increases again between 3.2 and 3.7. A total of sixteen fruticose lichens are represented by the data from 3.2 to 37. Close examination of the data in the region of interest shows that two of the samples were *Xanthoria elegans* from the Manti-Lasal National Forest which were collected from rock substrate. In addition, all eleven *Xanthoria polycarpa* lichens are in this region. These thirteen lichens account for the anomaly in fruticose species distribution.

As shown in Table 2, the Fe/Ti ratio is much higher for *Xanthoria polycarpa* than other species. Explanations for this pattern could be biological or environmental. No samples of this species were taken at any other site, so comparison on the basis of site is not possible. Some species of lichens are known to have an affinity for certain elements (*Dermatocarpon miniatum* for sulfur (5)), but data verifying selective binding of iron by *Xanthoria polycarpa* is incomplete.

Another possible explanation may be related to the presence of a steel mill in Utah county and the close proximity of the the sample sites to this facility. High concentrations of iron oxide have been reported in the air of Utah Valley. Another interesting trend is that the Fe/Ti ratios for foliose lichens in the same area seem normal. This fact suggests that airborne iron particles may accumulate to a greater degree in lichens which grow above ground level. Furthermore, as mentioned earlier, foliose lichens on rock substrate may be getting a larger fraction of their iron and titanium from the substrate. The eleven foliose lichens sampled in the same location have log[Fe] values ranging from 3.38 to 3.80, well within the general pattern for foliose species.

CONCLUSIONS

Elemental analysis of lichen tissues show a remarkably consistent relationship between iron and titanium. Our data show that the distribution functions of the log of iron concentrations for fruticose lichens is smaller than for foliose lichens. These relationships may be useful in identifying air pollution-related impact in the Rocky Mountain region.

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