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SR-XRF analysis of *Polytrichum* in the Fildes Peninsula, Antarctica

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Abstract In order to study the element contents and distribution of various mosses collected in the Antarctica, we analyzed the heavy elements of 3 species of *Polytrichum* in the Fildes Peninsula, *P. alpinum*, *P. juniperinum* and *P. alpestre*, by synchrotron radiation X-ray fluorescence (SR-XRF). The result shows that the elements, such as K, Ca, Mn, Fe, Cu, Zn and Sr, are nearly the same in *Polytrichum*. The peak intensity of K is higher than that of Ca, and the peak intensity of Ca is higher than that of Fe in *P. alpinum*. In *P. juniperinum*, the peak intensity of K is higher than that of Ca, and the peak intensity of Ca is close to that of Fe. The peak intensity of K is nearly equal to those of Ca and Fe in *P. alpestre*. Therefore, the habitats of 3 species of *Polytrichum* are similar in the Fildes Peninsula. By XRF analyzing of different parts of *P. alpestre*, we found that the peak intensities of relative concentration of elements are obviously different. The peak intensity of K in apical-bud is the highest in organism. The peak intensity ratio of K/Ca is 1.30, but they are below 1.0 in all the other parts. The peak intensity of Mn in pseudo-root is the highest in organism, and the peak intensity ratio of Mn/Fe is 0.21, the biggest. In the parts of older leaf and pseudo-root, the ratios of Cu/Zn are 1.20 and 1.84 respectively, whereas they are less than 1 in the other parts. The element Br is seen specially in the older leaf and pseudo-root, that may result from the organs aged, and enhance the ability of anti-rottenness itself.

Key words Antarctica, *Polytrichum*, heavy elements, X-ray fluorescence.

1 Introduction

The habitat of Antarctica is very special, only 5 percentage of land is uncovered by ice and snow in the King George Island. The vegetation of the Fildes Peninsula seems to be the best in development in the King George Island. The high moss flore, consisting mainly of Polytrichaceae, is the most remarkable and the most special vegetation in the Fildes Peninsula. They are growing on the volcanic foundation formed in modern times and are found often on the big gravel, the crushed stone pile and the moist sandy soil, which becomes a big dense cushion. In the Fildes Peninsula, *Polytrichum* grows from November to March of next year, but not from April to October (Wu *et al.* 1990).

Bryophyte is similar to vascular plant in the elements of mineral nourishment required. However, Bryophyte differs from vascular plant in the source of nourishment. The nourishment source of bryophyte is various, including soil, precipitation, air and rock surface. Generally speaking, the main source of nourishment in bryophyte is rather air than the foundation in which plant grows. The major way to obtain mineral nourishment depends on the classification of bryophyte. Owing to the presence of inner transfusion, *Polytrichum* possess a good system of inner transfusion and the cuticle to prevent evaporation, which can absorb proper nourishment and water from soil, or from precipitation and air. As one of the features to absorb nourishment, bryophyte possesses a very powerful ability which can absorb nourishment from the habitat with very low content and accumulate them (Wu 1998). Therefore, we studied the content and distribution of elements of the mosses in Antarctica, it is very useful for us to supervise environment pollution. Thanks to the very rareness and limited number of the specimen from Antarctica, we have selected SR-XRF which is a high speed analysis method without harm.

2 Materials and method

The plant specimens used in our experiments are *Polytrichum alpinum*, *P. juniperinum and P. alpestre* (Chen *et al.* 1994), collected from the Fildes Peninsula, the King George Island in Antarctica, Feb. 2000. The specimens were dried naturally, and stored in environment without any chemical treatment. The site of the collected specimens is shown in Fig. 1. Before experiment the specimens were watered 2 times by DI water.

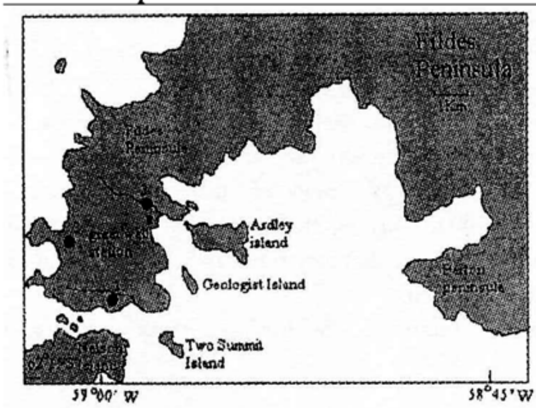

Fig. 1. The sketch map showing the site of the collected specimen.
1: *Polytrichum alpinum*; 2: *P. juniperinum*; 3: *P. alpestre*.

The XRF analysis was processed at 4W1A beam line, the Micro-beam Fluorescence Station of Beijing Synchrotron Radiation Facility (BSRF) at Oct. 2000. The advantages of synchrotron radiation can give us high sensitivity and good space resolution ability, without harm and pollution for specimen, and enable us to reuse specimen, under simple and convenient operation, or working in common condition and so on. SR-XRF is an ideal method for analysis of elements of bio-specimen (Zhang *et al.* 1996). The beam energy is 2.2 GeV, beam current is 100 - 40 mA, and the energy range of X-ray is 3.5 - 27.5 keV. The radiation area on specimen is controlled by slits. A Si (Li) detector and a 2048 multi-channel analyzer (MCA) with energy resolution of 150 - 350 eV are used for detection and spectrum analysis. The continuous spectrum X-ray that we used in our experiments is suitable for fast analysis of multi-elements simultaneously.

The specimen is fixed on the sample support. The distance between the specimen and the end-window of the beam-line is about 1 m. The angle is 90° between the detector and the incidence X-ray. The position of samples can be adjusted using an optical stereo microscope (Shen *et al.* 2001). The effective time of radiation is normalized to 400s at room temperature. The X-ray radiation area is fixed by $50 \times 60\ \mu m^2$ on the specimen.

3 Results and discussion

3.1 XRF spectra of the leaves of the 3 species of Polytrichum

The specimens of the 3 species of *Polytrichum* came from the middle part of the stems respectively, the spectra are shown in Fig. 2. According to present analysis, more than 20 kinds of element in bryophyte, K, S, B, Ca, Cu, Fe, Mn, Mg, Na, Ni, Ti, Zn, Sr, Si, P, Pb and so on are detected (Wu 1998). However, we have only examined the elements Cl, Ar, K, Ca, Mn, Fe, Cu, Zn and Sr in the three XRF spectra. The light elements like Na, Mg, etc. can not be examined due to the absorption of Be window of detector and the air on the path. From the shape of XRF spectra, the elements and contents in the leaves of the 3 species of *Polytrichum* are very close to each other, which show that their habitats are similar. However, by analyzing carefully every element peak intensity of XRF spectra, we found that there still are difference with three specimens.

POLYTRI1 is an XRF spectrum of *P. alpinum*. The peak intensity of K is far high than that of Ca. K exists mainly in the cell sap but not in the composition of cell. Ca exists mainly in the cell wall with exchangeable form. The high content of the element K shows that *P. alpinum* possesses more vigorous metabolism. Furthermore, the spectrum peak intensity of Ca is higher than that of Fe. POLYTRI2 is an XRF spectrum of *P. juniperinum*, in which, the peak intensity of K is clearly higher than that of Ca, while the peak intensity of Ca is nearly equal to that of Fe. POLYTRI3 is an XRF spectrum of *P. alpestre*. Little difference is found in the peak intensities of K, Ca and Fe. However, comparing with two spectra above-mentioned, the peak intensity of Mn becomes clearly high, which increases the ratio of Fe and Mn. There are 2 types of the element Fe in plants, functional compound to possess Fe-S-protein and store compound to possess Fe-protein. There are many enzymes in plants, for example, oxidase, reductase, nitrogenase, hydrase, peroxidase, hydrogenase and catalase. Combined with the chlorophyll molecules in some proportion in plants (about 400 molecules of the chlorophyll combined with 6 - 8 atoms Mn), the element Mn is still a cofactor or activator which are controlled by enzyme in reaction. Generally, the amount of the element Mn is half of the element Fe in plant needed. According to the XRF spectra, the element Mn may reduce further more in bryophyte.

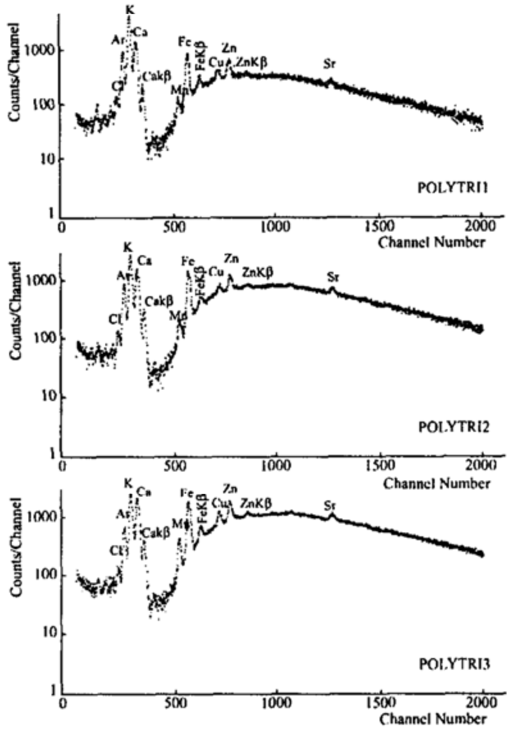

Fig. 2. The spectra of XRF of leaf in 3 species of *Polytrichum*.
POLYTRI1 *Polytrichum alpinum* (beam current 97.1mA).
POLYTRI2 *P. junipericum* (beam current 96.4 mA).
POLYTRI3 *P. alpestre* (beam current 95.8 mA).

3.2 XRF spectra of different parts of Polytrichum alpestre

In order to study the element distribution of bryophyte in Antarctica, we analyzed the XRF spectra of the apical - bud, older leaf and older stem of *P. alpestre*, and results are showed in Fig. 3.

At present, the XRF analysis method is mainly qualitative analysis. The quantitative analysis method is rather difficult because there are no standard samples utilized (Hayat1980; Jones and Gordon 1989). Under normal condition, the fluorescence peak intensity can be expressed directly as the element content (Li *et al.* 1999). The relative concentrations of major elements (by peak intensity) of *P. alpestre* are listed in Table 1.

As in vascular plant, the mineral nourishment elements not only are effectively absorbed, but also can be transferred into the organism of bryophyte in the older parts to the apical growing part.

It is obvious in Table 1 that the peak intensities of K in the apical - bud (POLYTRI6) and in the functional leaf (POLYTRI3) of *P. alpestre* are very high, and the ratios of K/Ca are 1.30 and 1.13, while the ratios of other parts are all below 1.00. Although K is not component of the cell, it is important to maintain the metabolism of the cell. In the apical - bud, the relative content of Zn is higher than the element Fe (Zn/Fe = 1.25), and Zn is nearly equal to that of Fe (Zn/Fe = 0.81) in the functional leaf. A large number of Zn exist in the young tissue, which shows that the metabolism is vigorous. Because there is Zn in transferring enzyme, polymerase, hydrolase, isomerase and oxido-reductase, and Zn re-

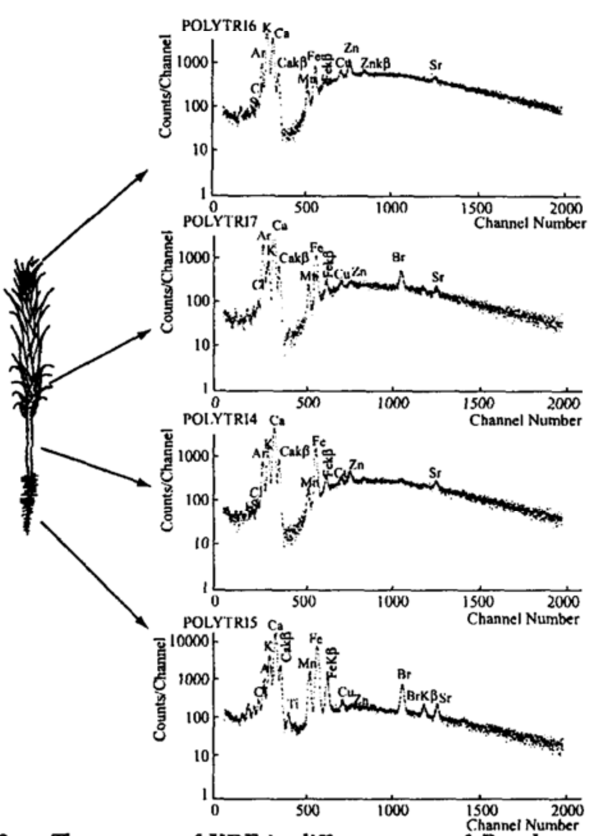

Fig. 3. The spectra of XRF in different parts of *P. alpestre*.
POLYTRI6 apical - bud, beam current 90.6mA; POLYTRI7 older leaf, beam current 89.9mA; POLYTRI4 older stem, beam current 94.9mA; POLYTRI5 pseudo-root part, beam current 91.1mA.

sists both Cu and Fe, so a high content of Zn will control and reduce the content of Fe.

Table 1. The relative concentration of element in different parts of *P. alpestre*

Element	Apical - bud	Functional leaf	Older leaf	Older stem	Pseudo-root part
K	60857	39776	8206	20779	54460
Ca	46968	35241	41183	62873	211561
Mn	2925	4713	1952	1557	23169
Fe	9350	26675	10048	17641	113008
Cu	5986	12957	2217	2922	2675
Zn	11543	21454	1850	3721	1453
Br	—	—	685	—	11111
Sr	1067	4085	459	1253	2484

In the XRF spectra of the older leaf (POLYTRI7) and the pseudo-root (POLYTRI5), the relative concentration of Cu increases clearly, and it results in that the ratios of Cu/Zn are up to 1.20 and 1.84, while the ratios are less than 1.00 in the other parts. The element Zn is present mainly as the state of carbonic anhydrase, lactate dehydrogenase, and glutamate dehydrogenase, which may lead to assimilation. The element Cu is the component of nitrite reductase and polyphenol oxidase, it mainly appears as a action of dissimilation. Therefore, both the older leaf and the pseudo-root are the organs aged (pseudo-root is a single cell, growing continuously of the upper ones, but dying constantly of the lower ones). The relative content of Cu is higher than that of Zn. In addition, two aged organs of *P. alpestre* have element Br, as shown in pseudo-root spectrum. The element Br in organic compound possesses a vitality of germ-resistant and bacterium-resistant. In the organ aged, the element Br may be related to the strong ability of anti-rottenness itself.

In all XRF spectra of *P. alpestre*, the relative concentration of the element Ca is rather stable. Because the ion Ca^{2+} maintains mainly the construction of many cells and takes part in the composition of cell wall.

Based on the discussion above, it is obvious that the distribution and the relative content of mineral elements are various in different parts of bryophyte. As one-valence element, K exists mainly in the cell sap, and two - valence element Ca exists mainly in the cell wall with exchangeable form. Mn, Cu and Zn are inter-mediate state and exist in the organelles. The interrelated studies have shown that Cu, Mn, Zn and Ca can be stored in the nucleus, mitochondria, lysosome, vacuole system and some sub-cell units, which can prevent these elements from affecting the enzyme system of the cytoplasm. As a result of that, the elements of heavy metal are stored and detoxified (Wu 1998).

4 Conclusion

By means of the study of XRF spectra about the leaves of the 3 species of *Polytrichum* in the Fildes Peninsula, we found that the spectra are clearly different. However, the shapes of XRF spectra are similar in same genus. The distribution of the elements in bryophyte is different along with the age of the organ and in different parts of *P. alpestre.*

Generally, one-valence element tends to be gathered more at the growing part, so the content of K is highest in the young tissue. Two-valence element is accumulated along with the development of the organ, so that the content of the elements Ca, Mn and Fe will increase accompanying the growth of plant. The difference of the element content depends on the distribution of various elements in bryophyte, which may be related with the active absorption and the transfusion speed of some elements in bryophyte.

Comparing with other elements in *P. alpestre*, the content of Ca is more stable in various parts, but content of K is quite changeable. When the organ of *Polytrichum* tends to be aged, the plant will actively absorb element Br from its habitat to enhance the ability of anti-rottenness itself.

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