Feasibility of using reflectance spectroscopy for the analysis of bio-element concentrations in Antarctic ornithogenic sediments

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Abstract　　Compared with traditional chemical analysis methods，reflectance spectroscopy has the advantages of speed，minimal or no sample preparation，non-destruction，and low cost. The present study explored the application of the reflectance spectroscopy within near ultraviolet-visible-near infrared region to predict bio-element compositions in the ornithogenic sediments from the maritime Antarctic. A total of 106 samples were taken from four ornithogenic sediment cores on the Ardley Island of Antarctica，68 samples were used for building calibration equation，and 38 for prediction of nine bio-elements including P，Ca，Cu，Zn，Se，Sr，Ba，F and S. Three multivariate statistical analysis techniques，including stepwise multiple linear regression (Stepwise-MLR)，principal component regression (PCR) and partial least squares regression (PLS) were used to develop mathematical relationships between the spectral data and the chemical reference data. The results showed that the regression models constructed by PCR and PLS models have no significant differences，and obviously supervisor to Stepwise-MLR. The correlations between spectra-predicted and chemically analyzed concentrations of nine bio-elements are statistically significant，and the concentration-versus-depth profiles predicted from reflectance spectra using PLS calibration model are consistent with those from actual chemical analysis. These results demonstrated the feasibility of using reflectance spectroscopy to infer bio-element concentrations in the ornithogenic sediments，and thus it is suggested that the reflectance spectroscopy could provide a rapid and valuable technique to indirectly identify whether the sediments were influenced by penguin droppings in the Antarctic region.

Key words　　Reflectance spectroscopy，Ornithogenic sediments，Multivariate statistical analysis，Bio-element，Antarctic.

1　Introduction

Reflectance spectroscopy，a non-destructive technique，has been considered as an alternative or complementary method for compositional analysis of various chemical constituents in soil，sediment and biological samples，and for assessment of environmental quality[1-12]. Recently，there is a growing interest in using reflectance spectroscopy for palaeolimnological and palaeoenvironmental studies，since this method offers several special advantages such as speed of determination，minimal or no preparation of samples，non-destructive analysis，no consumption of reagents，and low costs of analysis[13-22].

Wavelength position and height of the spectral peaks from reflectance spectroscopy cannot directly be used for determinations of chemical compositions，because the spectra are too complex and the peaks in the near infrared region are broad and overlapping. Instead，the spectra have to be calibrated using samples in which the constituents of interest are known from reference methods. Useful information from the spectra can be extracted using chemometric techniques such as stepwise multiple linear regression（Stepwise-MLR）or other multivariate calibration methods such as principal component regression（PCR），and partial least squares（PLS）regression[23].

In recent years，numerous studies showed that the remnants of ancient penguin droppings in the lake sediments near penguin colonies may be identified by their geochemical characteristics，which may provide continuous information about historical population changes of penguin[24-29]. Nine elements including sulfur（S），phosphorus （as P_2O_5），calcium（as CaO），copper（Cu），zinc（Zn），selenium（Se），strontium （Sr），barium（Ba）and fluorine（F）have been found to be enriched and significantly correlated with each other in the sediments amended by penguin guanos，and their assemblage is identified to be an important geochemical signal for indication of impact from penguin droppings or guano soils in Antarctica[24][30]. Besides these elemental proxies，isotopic and organic geochemical proxies have also been successfully used to reconstruct the long-term variations in historical penguin populations[31-33]. Since these multi-proxies are usually not determined on the same aliquot and the samples are taken from remote Antarctic areas，there is a common trouble of insufficient amount of samples for chemical analyses in the laboratories. Therefore，there is a need for faster and more efficient and economical methods to facilitate reconstruction of palaeorecords in the Antarctic ornithogenic sediments and to improve the understanding of the effects of climate change on penguin ecology.

According to the issued reports，reflectance spectroscopy has rarely been used for scientific research in maritime Antarctic. In this paper，four sediment cores influenced by penguin droppings on the Ardley Island were selected and the corresponding reflectance spectroscopy signals were analyzed with the main objective to examine the feasibility of using reflectance spectroscopy within near ultraviolet-visible-near infrared region to determine nine bio-elements concentrations in the sediments. If this can be done successfully，reflectance spectroscopy will allow numerous chemical constituents in core sections to be determined rapidly and simultaneously，and thus greatly reduce the cost for certain chemical analyses. Thus，in the future this approach may provide a rapid technique to identify whether the sediments are impacted by penguin

droppings in the Antarctica, and further to reconstruct the palaeoecological evolution recorded in the Antarctic ornithogenic sediments.

2　Study Area

The Ardley Island (62°13′S, 58°56′W), a 2 km long and 1.5 km wide island, is about 500 m to the east of Fildes Peninsula, Maxwell Bay, King George Island and connected with the Fildes Peninsula by a sandy dam (Fig. 1). The Great Wall Station of China is located about 0.5 km to the west of the island. The study area has a cold oceanic climate, characteristic of maritime Antarctica. According to the meteorological records from the Great Wall Station, the mean annual precipitation is about 630 mm, the annual average relative humidity is about 90%, and the mean annual air temperature is around -2.6 ℃ with a winter low at -26.6 ℃, and summer high at 11.7 ℃. It is free of snow and ice during the summer. Geologically, the island mainly consists of tertiary andesitic and basaltic lavas and tuffs together with raised beach terraces. The topography of the island is relatively flat with the highest elevation of 70 m. Seventy-eighty percent of the island is covered by vegetation, predominantly consisting of mosses and lichens.

Ardley Island is one of the most important penguin colonies in the maritime Antarctic region. In 1991, this island has been declared as Antarctic Specially Protected Area by the Protocol on Environmental Protection to the Antarctic Treaty. During the breeding period every summer, the number of penguins on this island was about 10218; the major species were Gentoo (*Pygoscelis papua*, 74%), Adelie (*Pygoscelis adeliae*, 21%) and Chinstrap (*Pygoscelis antarctica*, 5%)[31,34]. It is estimated that penguins on the Ardley Island discharge about 139 t droppings based on the hypothesis that each penguin excretes 84.5 g droppings (dry weight) a day during the breeding period[27,30]. Droppings are transferred and deposited in the lakes or depressions by ice or snowmelt water, and those ancient penguin waste products preserved in the sediments record the historical information of penguin population change[24].

3　Materials and Methods

3.1　Sample collection and chemical data

A total of 106 samples were collected from four sediment cores (Y2, Y2-4, Y4 and AD3) on the Ardley Island for spectral and chemical analyses. For comparison, 5 soil samples (N1) and 3 pure guano samples (AP) were analyzed for spectral characteristics. The sampling sites of four sediment cores are shown in Figure 1. The sediment cores Y2 and Y2-4 are collected from the same lake Y2. The lithological descriptions of these sediment cores are given in the references[24,28,30], in which studies have showed that all the sediment cores are influenced by penguin droppings. In the laboratory, the sediment cores were sectioned at the intervals of 1-2 cm, and the subsamples were air-dried, sieved and then ground to powder for chemical analysis. The chemical methods, as well as the concentrations of nine bio-elements including S, P,

Ca, Cu, Zn, Se, Sr, Ba and F in the sediment subsamples, are reported in detail in the references mentioned above. The soil samples(N1) were affected neither by penguin droppings nor by biological action, and they are natural products of local bedrock weathering[35].

3.2 *Spectral measurement and transformation*

Prior to spectral analysis, the collected sediment subsamples were ground in a mortar
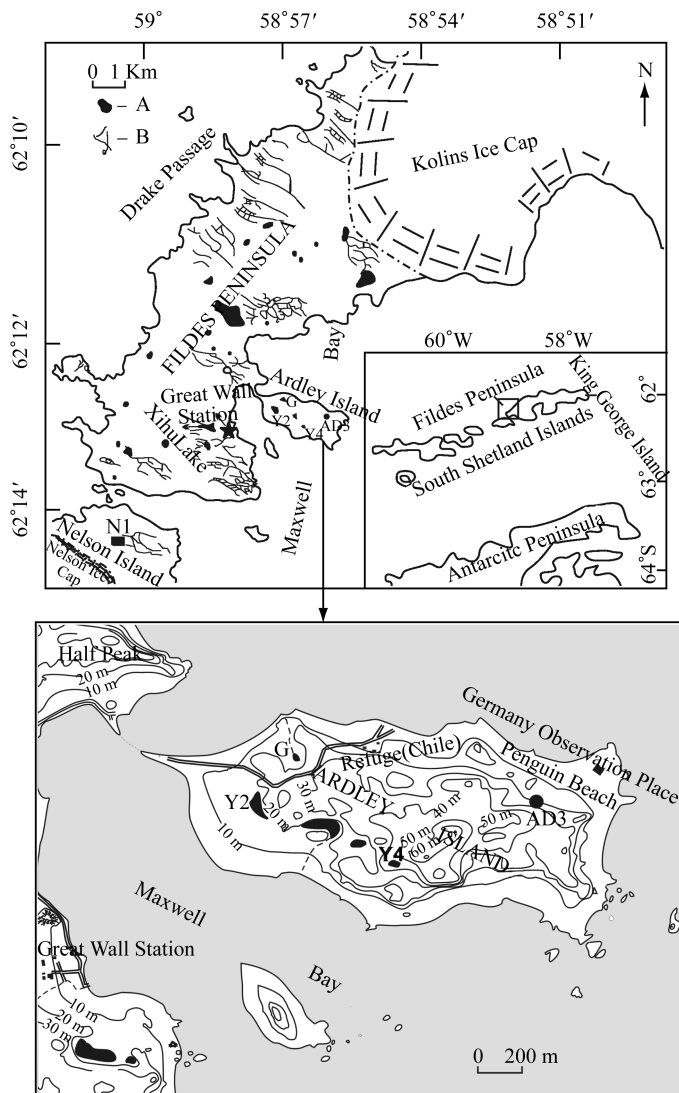
Fig. 1　Studied area and sampling sites (Y2, Y4 and AD3). In the top panel, marker A shows lakes, marker B shows network of meltwater channels. In the bottom panel, the contour interval is 10 meter (From Liu *et al*. 2005).

to pass a 0.074 mm sieve, and then dried at 105 ℃ for 2 hours. For each sample, approximately 1 g powder was packed into a measuring cell, and subsequently the spectral reflectance was recorded in Shimadzu SolidSpec-3700 UV-VIS-NIR Recording Spectrophotometer, configured with UV-Probe software. All the samples were scanned over a wavelength range of 200-2600 nm covering the near ultraviolet-visible-near infrared region at 1 nm interval. A total of 2401 data points were collected for each spectrum and it took less than 10 minutes to complete a scan. Samples were read against an external polyethylene (zero absorbance) reference, which was read alternately with the samples. The reference spectrum was automatically subtracted from each sample spectrum and the resulting spectrum automatically recorded. To

establish a robust prediction model，several spectral pretreatments were applied to the reflectance spectra to optimize the accuracy. Using UV-Probe software，the original reflectance (r) data could be transformed to first (r') or second (r'') derivative，reciprocal (1/r) and absorbance (log 1/r) data.

3.3 *Model construction and validation*

To establish and test mathematical relationships between spectral data and the corresponding chemical reference data，two sets of samples were created firstly：calibration set and prediction set. For each chemical constituent，stepwise multiple linear regression，principal component regression and partial least squares regression methods were used to find and test the mathematical relationship，then their calibration results were compared.

The first method is stepwise multiple linear regression (Stepwise-MLR). Considering that the reflect peaks (or absorb valleys) are the most significant (see below)，the reflect peaks of each spectra curve and removed the overlapping ones were picked out. A total of 121 peaks were selected to perform the regression analyses and establish the mathematical relationship between these independent variables with reference chemical data，the dependent variables. Five mathematical regression equations using the independent variable of the raw optical data (r) and four derived data (r', r'', 1/r, log(1/r)) and the calibration data set were computed by the Stepwise-MLR option of MATLAB 7.1；r' and r'' represent the first and second order derivatives of r. These computations generated a number of statistical parameters such as R^2 (square of the regression coefficient) and RMSE (root mean squared error of calibration) [18]. The regression equations from the calibration data set were used to predict the relevant chemical constituents of the prediction set. The predicted values were compared with the measured reference values using several statistics，such as R，the coefficient of linear correlation，and SEP，the standard error of prediction (the standard deviation of the points about the 1：1 line). For each constituent，the regression equation yielding the highest R and the lowest SEP was accepted as the best ones. The regression equation was further evaluated by two additional statistical quality parameters：the residual predication deviation (RPD) and ratio error range (RER). The RPD is the ratio of the standard deviation (SD) of the reference chemistry values for the prediction set over the SEP. The RER is the ratio of the range of the reference chemistry values in the prediction set over the SEP. In agricultural applications，RPD values >5 are desirable，>3 are acceptable，and between 2.5－3 are suitable for screening；RER should be greater than 10[16,17].

The second method，principal component regression (PCR) is a two-stage process. First，it minimizes the number of independent components required to describe the variations over the entire spectrum and between spectra. This technique enables a total of 2401 spectral points to be reduced to a few principal components (PCs)，where the PCs describe the spectral variance over all the samples. Second，these PCs are regressed against known property data (measured concentration)，and then regression models are constructed. In this study，the method of singular value

decomposition (SVD) in MATLAB 7. 1 were used and the method of "validation set prediction" was chosen to evaluate the precision of regression[36]. Regression models were further evaluated by the statistic parameters mentioned above.

The third method，partial least squares regression（PLS），is widely used for multivariate calibration and has been applied in various applications for chemical analysis. PLS decomposes spectral data（X）and sediment property data（Y）into a new smaller set of latent variables and their scores that best describe all the variance in the data[3]. PLS was performed using ParLeS software version 3. 1，which is specially designed for chemometric analysis of spectroscopic data[37]. In the present study the same optimal spectral indices was used as PCR. Following the procedure of Malley *et al*. (1999)[16]，cross validation，also known as 'jackknifing' or 'leave-one-out'，was used to pick out the best number of factors for regression. The PLS can be performed to maximize the size of the calibration data set and to predict all of the samples. It used the mathematical treatment and number of PLS factors from the previous steps to develop calibrations. The procedure was repeated 68 times until each sample is predicted. Regression models were further evaluated by the statistics mentioned above（R，SEP，RPD and RER）to ensure they are robust enough for predicting concentration data of nine bio-elements from the reflectance spectral.

4 Results and discussion

4. 1 *Distributions of elements and spectral characteristics*

Reflectance spectra of representative samples from the four ornithogenic sediment cores are given in Figure 2. It can be seen from this figure that the shape of the spectra curves is almost identical for all four samples，but the reflectance values are notably different. All the ornithogenic sediments have high reflectance intensity in the near-infrared light region（800－2500 nm）. The ornithogenic sediments are predominately composed of the weathering products from bedrocks and the penguin guano，and the guano contains much more organic matter than the weathering products，thus the input of penguin guano could significantly influence the content of organic matter in the sediments[26,32]. Numerous studies have shown that the attributes of organic materials are important for NIR spectral feature [18,20]. It is assumed that the penguin guano enriched with organic matter is the dominant influencing factor on the reflectance spectra of these ornithogenic sediments.
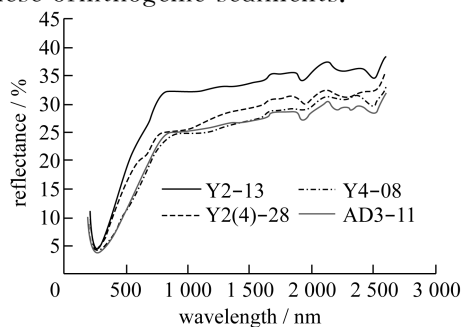
Fig. 2   Reflectance spectra of representative samples from the four sediment cores.

Some trace elements in sediments and soils generally do not respond to the incident light directly，but they may be detectable in the spectrum signatures because they can form complex with organic matter，and be associated with moieties such as hydroxides，sulfides，carbonates or oxides that are detectable，and be absorbed to clays that absorb light in some wavelength range[2,8,20]. Sun *et al.* （2000，2001，2004）[24,25,30] reported that nine inorganic elements including S，P，Ca，Cu，Zn，Se，Sr，Ba and F were enriched and significantly correlated with each other in the soils or sediments amended by penguin guanos. The assemblage of P，Sr，Cu，Zn，Se，Ca，F，Ba and S is suggested to be an important geochemical marker for penguin droppings or the soils and sediments impacted by them in the maritime Antarctic. Thus，it can be reasonably inferred that the reflecting intensity of the ornithogenic sediments is related to the concentrations of the nine bio-elements.

In this study，the spectra data that represent the same data sets for all the nine bio-elements were chosen. Using the same procedure for chemical data processing，spectra are sorted from lowest to highest reflectance values and divided into two groups. Two-thirds of the spectra were used as a calibration set，and the remaining as a predication set. Each set represented approximately the full range of concentrations. Two-thirds of the spectra were used as calibration set，the rest as predication set，and they consist of 68 （except for element Ba，n＝67） and 38 samples，respectively. Chemically determined concentrations of nine bio-elements （P_2O_5，CaO，Cu，F，Ba，S，Zn，Sr，and Se） in both sets are given in Table 1，and they are of large variations，indicating variable influence of penguin droppings on the sediments [24,28]. The values of standard deviation （SD） and range are used to compute the statistic of RPD and RER in the model calibration，respectively.

Table 1.   Chemically determined concentrations of nine bio-elements in the calibration and prediction sets

Element	Units(g/g)	set	min	max	mean	range	SD	n
P_2O_5	10^{-2}	Cal	0.74	15.52	6.372	14.78	3.688	68
		Pred	0.64	13.45	6.472	12.81	4.339	38
CaO	10^{-4}	Cal	5.23	19.80	9.931	14.57	3.453	68
		Pred	5.18	18.35	10.304	13.17	4.455	38
Cu	10^{-4}	Cal	0.62	9.95	3.600	9.33	2.105	68
		Pred	0.65	7.65	3.619	7.00	2.335	38
F	10^{-4}	Cal	3.92	123.90	40.200	119.58	27.690	68
		Pred	3.21	83.13	38.037	79.92	28.501	38
Ba	10^{-4}	Cal	0.93	2.54	1.635	1.61	0.474	67
		Pred	0.95	2.42	1.509	1.48	0.404	38
S	10^{-4}	Cal	1.40	178.00	38.990	176.60	42.520	68
		Pred	1.30	18.40	52.550	182.70	57.360	38
Zn	10^{-4}	Cal	0.52	8.35	3.424	7.83	2.010	68
		Pred	0.35	7.52	3.447	7.17	2.367	38
Sr	10^{-4}	Cal	3.69	19.30	9.191	15.61	4.779	68

		Pred	3.84	18.46	9.163	14.62	5.422	38
Se	10^{-6}	Cal	1.44	54.90	17.823	53.46	14.905	68
		Pred	1.69	49.70	18.716	48.01	17.772	38

4.2 *Construction of calibration models*

Table 2 summarizes the results of optimal Stepwise-MLR model and statistical parameters. As shown in this table, the prediction quality strongly depends on data preprocessing. For example, the best results were achieved using first order derivative (r') for Sr, Cu and Se, reciprocal ($1/r$) for S and Zn, and original spectra (r) for P_2O_5 and Ba. The optimal models achieved high precisions of regression and validation for each bio-element, and all the coefficients of regression calibrations, R^2, are close to or exceed 0.95. The correlation coefficients, R, between the reflectance spectrum predicated and chemically determined concentrations is higher than 0.95, except for Ba (R=0.894). RPD are >2.5 for most elements, and RER are >10 for P, Ca, Cu, F, S and Zn. The wavelengths upon which the Stepwise-MLR calibrations are based are listed in Table 2, they indicate the regions of the spectrum used in the prediction, and are different for each element. This result is consistent with the observations by Malley *et al*. (1999)[16] and Malley and Williams (1997)[2]. Generally, the results of model reconstruction by the Stepwise-MLR calibration are satisfactory for most bio-elements, indicating that the spectral method has potential to predict rapidly the concentrations of nine bio-elements in the ornithogenic sediments in the maritime Antarctic.

Table 2.   Prediction accuracy, mathematical treatments model, and used wavelengths for the determination of nine bio-element concentrations by stepwise-MLR

Element	P_2O_5	CaO	Cu	F	Ba	S	Zn	Sr	Se
R^2	0.983	0.963	0.973	0.981	0.947	0.955	0.961	0.933	0.948
RMSE	0.523	0.713	0.375	4.060	0.121	9.424	0.415	1.333	3.583
R	0.962	0.972	0.971	0.963	0.894	0.976	0.969	0.951	0.959
SEP	1.179	1.059	0.578	7.686	0.192	11.902	0.588	1.630	5.611
RPD	3.681	4.209	4.043	3.708	2.107	4.819	4.026	3.327	3.167
RER	10.868	12.442	12.120	10.398	7.692	15.351	12.194	8.970	8.556
Model	r	$\log 1/r$	r'	$\log 1/r$	r	$1/r$	$1/r$	r'	r'
Wavelength/nm	844	669	669	654	260	654	654	844	844
	876	1720	844	844	669	669	669	1407	866
	1730	1916	929	1021	844	844	1720	1715	1400
	1741	1934	1400	1916	1021	859	1838	1724	2250
	1855	2108	1709	1939	1916	1846	2409	2213	2346
	1922	2132	1720	2209	2102	2144	2491	2230	2351
	1939	2213	2102	2400	2235			2346	2504
	2209	2480	2292	2495	2240			2367	
	2400	2487	2351	2510	2245			2427	
			2510		2250				

2363

2395

The statistical parameters of the final models using the PCR method are summarized in Table 3. Calibrations developed by PCR for all bio-elements produced good relationships with Rs>0.92 and RPDs>2.5. Most RER values are beyound 10 except for Ba. Compared with the results of Stepwise-MLR calibrations (Table 2), PCR calibrations have the higher correlation coefficients Rs, lower SEPs, larger RPDs and RERs for the same inorganic element. Thus, PCR calibrations utilizing the whole spectrum data (2401 spectral points) were clearly superior to Stepwise-MLR characteristic of segmental spectra analyses.

Table 3.   Regression statistics and parameter estimates for the determination of nine bio-element concentrations by PCR method

element	P_2O_5	CaO	Cu	F	Ba	S	Zn	Sr	Se
units	10^{-2}	10^{-2}	10^{-4}	10^{-4}	10^{-4}	10^{-4}	10^{-4}	10^{-4}	10^{-6}
Model	r	log 1/r	r′	log 1/r	r	1/r	1/r	r′	r′
R	0.978	0.983	0.977	0.975	0.924	0.984	0.987	0.979	0.963
SEP	0.890	0.862	0.496	6.105	0.161	9.875	0.374	1.094	4.668
RPD	4.876	5.171	4.710	4.668	2.513	5.809	6.322	4.955	3.807
RER	14.395	15.287	14.119	13.090	9.176	18.501	19.150	13.360	10.284

Table 4 summarizes the statistic parameters for PLS calibration. The predicted concentrations by PLS for P_2O_5, CaO, Cu, F, S, Zn and Sr have Rs>0.97, RPDs>4.0 and RERs >12, indicative of good calibrations. The calibration for Se gives R of 0.956, RPD of 3.472 and RER of 9.381. The poorest calibration is for Ba, it gives a high correlation coefficient R of 0.914, but both the RPD at 2.421 and RER at 8.842 are lower than desirable. Compared with the results of Stepwise-MLR calibrations (Table 2), PLS calibrations have higher correlation coefficients Rs, lower SEPs, larger RPDs and RERs. Thus, PLS calibrations utilizing whole spectrum data (2401 spectral points) are also clearly superior to Stepwise-MLR calibration method. Compared with the result of PCR calibrations, it is found that the differences among the statistics R, SEP, RPD and RER are very small. Due to the overlapping of absorption peaks and the collinearity of the absorbance at different wavelengths, methods using single wavelengths such as Stepwise-MLR are usually less successful than principal component regression (PCR) or partial least squares regression (PLS), which utilize the whole spectrum to extract the spectral fingerprint of a chemical compound. Therefore, it is suggested that the reflectance spectral method utilizing mathematical treatment models PCR and PLS has the potential to rapidly predict the concentrations of nine bio-elements in the ornithogenic sediments of the maritime Antarctic.

Table 4.   Mathematical treatment model, optimal number of factors, and prediction statistics for the determination of nine bio-element concentrations by PLS

Element	P_2O_5	CaO	Cu	F	Ba	S	Zn	Sr	Se

Model	r	log 1/r	r′	log 1/r	r	1/r	1/r	r′	r′
No of factors	17	16	7	14	9	10	10	8	8
R	0.976	0.973	0.972	0.975	0.914	0.982	0.987	0.977	0.956
SEP	0.953	1.035	0.542	6.196	0.167	10.363	0.386	1.132	5.118
RPD	4.555	4.302	4.305	4.600	2.421	5.535	6.127	4.790	3.472
RER	13.447	12.719	12.905	12.899	8.842	17.631	18.56	12.916	9.381

Figure 3 gives loadings of the first factors of reflectance spectral data from PLS vs. wavelength for nine bio-elements. The loadings indicate wavelength regions where variance was used in computing the PLS calibration equations. The results showed that the first PLS factor for all nine bio-elements account for the vast majority of the variance in their concentrations (93%, 87%, 88%, 96%, 87%, 82%, 59%, 90%, 73% for Ba, Zn, P_2O_5, CaO, Cu, F, S, Sr and Se, respectively) and the loadings are virtually identical (Fig. 3). This indicates that the organic matter from the penguin droppings responsible for the variability in the bio-element levels is of the same quality for all bio-elements[2]. Furthermore, for all nine bio-elements, the loading versus wavelength profiles of the first factor are very consistent with those curves of reflectance spectrum of the sediment samples (Fig. 2), and this confirms that the reflectance spectrum intensity of the ornithogenic sediments is predominantly controlled by the concentration changes of nine bio-elements, which depend on the amount of penguin dropping input.
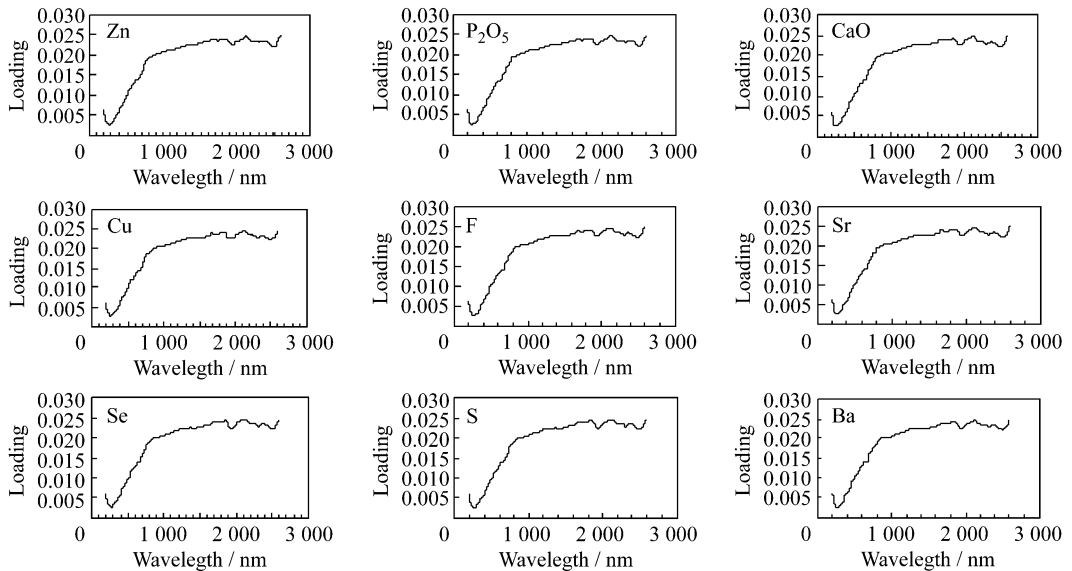

Fig. 3   Loadings of the first factor of reflectance spectral data from PLS vs. wavelength for nine bio-elements.

4.3   *Comparison of NIR-predicated and reference bio-element concentrations*

As suggested previously, PLS has advantages in reducing noise, detecting the compositions of unknown samples that are not represented by the calibration model,

and obviating the need for wavelength selection; and it tends to improve model stability and increase prediction accuracy[3]. Therefore, up to now PLS is widely used for multivariate calibration and chemical analysis. In present, the calibration equations constructed by PLS approach were used to predict chemical constitutes of each sample for the cores Y2 and Y4, and then compare NIR-predicated and reference core profiles.

The reference concentration data of nine bio-elements in the ornithogenic sediments and those predicated by PLS on UV-VIS-NIR are compared in Figure 4. As shown in this figure, the slopes of the measured vs. predicated regression lines for all the nine bio-elements are not significantly different from 1, indicating that this technique does not over or underestimate the chemical properties of ornithogenic sediments.

To visually compare the concentration-versus-depth profiles determined by reference chemistry and reflectance spectral methods, the concentrations of nine bio-elements in all the subsamples from the sediment cores Y2 and Y4 were computed using the PLS calibration
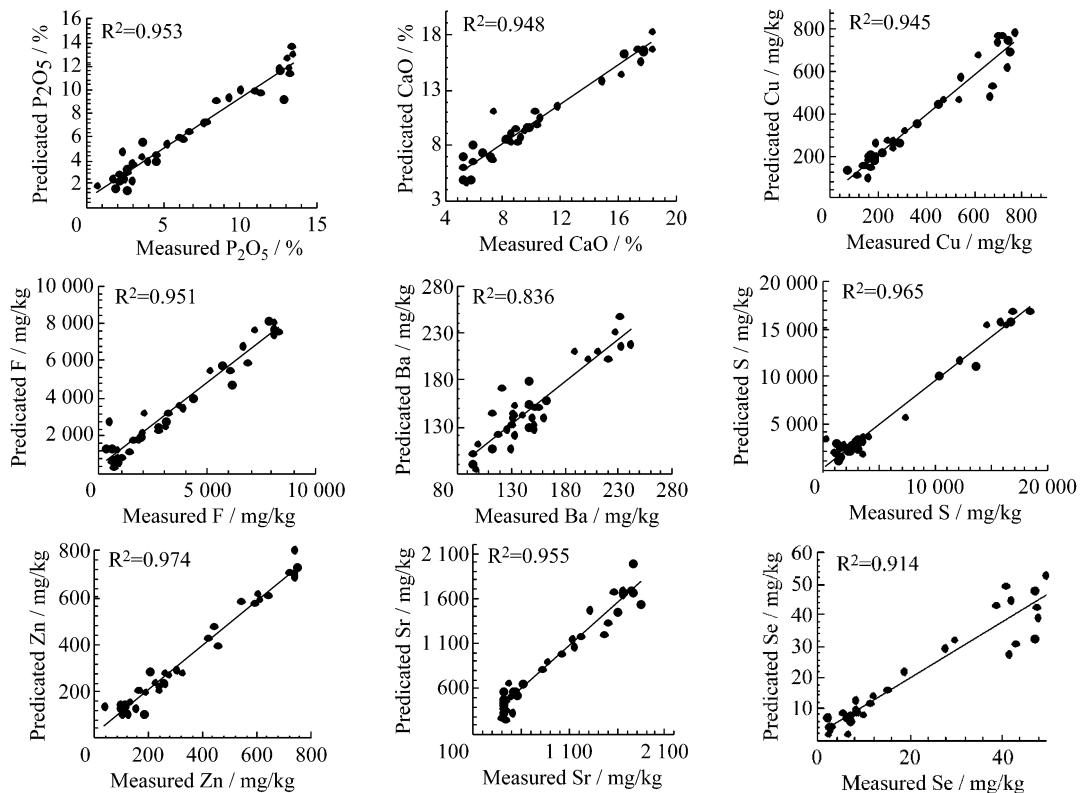

Fig. 4　Correlations between the concentrations determined by PLS and reference chemistry of nine bio-elements.

model. The measured and inferred values for Y2 and Y4 sediment cores are plotted versus depth in Figure 5 and Figure 6, respectively. As shown in these two figures,

with the exception of Ba in Y4 (Fig. 6), which has a relatively low correlation coeffi-
cient of 0. 35 (p>0. 01), all the reflectance spectrum-predicated profiles of nine bio-
elements are significantly correlated with those by chemistry reference (p<0. 01).
This implies that the overall trends in bio-element concentrations in the ornithogenic
sediment cores on the Ardley Island can be reconstructed from reflectance spectrum
without chemical measurements. For Ba in the core Y4, the marked difference is
likely due to the fact that Ba in the Y4 lacustrine sediments is associated with litho-
genic elements, not bio-source ones[28].

5 Conclusions

In this paper, four Antarctic ornithogenic sediment cores were taken as study
samples, and measured by both chemical and spectral methods. Based on the Step-
wise-MLR, PCR and PLS approaches, mathematical relationships between the spec-
tral and the chemical reference data were developed. The correlation structure re-
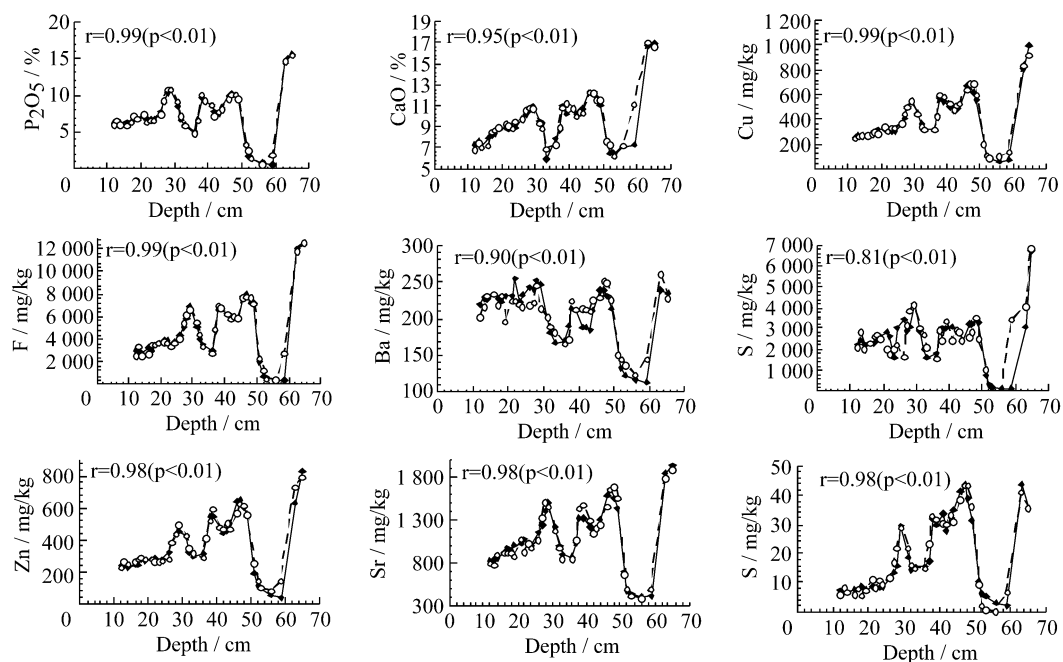flects clearly the prediction results:

Fig. 5 Comparison of concentration versus depth profiles determined by reference chemistry (solid dot
line) and PLS-predicted by reflectance spectroscopy (hollow dot line) for nine bio-elements in the
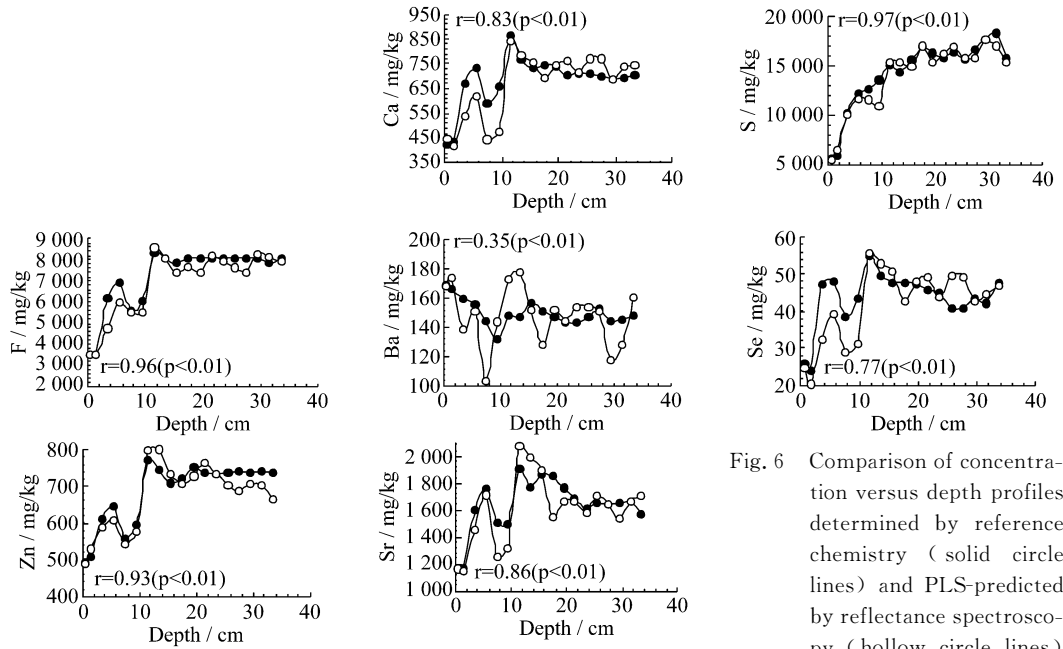Y2 core.

Fig. 6　Comparison of concentration versus depth profiles determined by reference chemistry （ solid circle lines） and PLS-predicted by reflectance spectroscopy （ hollow circle lines） for nine bio-elements in the Y4 lacustrine sediments.

the reflectance spectra of the sediments are significantly correlated with the nine bio-element concentrations（S，P，Ca，Cu，Zn，Se，Sr，Ba）and these elements are predicted more precisely by PCR and PLS. The correlation coefficients between PLS-predicted and chemically analyzed concentrations of these nine bio-elements are very high，and the predicated concentration-versus-depth profiles were very consistent with those from actual chemical analysis. These results demonstrated that it was feasible to predict bio-element compositions in the maritime Antarctic using the rapid，cost-effective，non-destructive and simultaneous technique of reflectance spectroscopy. Thereby this technique has the potential of being a valuable tool for the palaeo-ecological process study of penguins，other seabirds and mammals in Antarctic region through augmenting sampling density.

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