Analysis of the Mineral Composition of Taro for Determination of Geographic Origin

Natsuko I. Kobayashi,[†] Keitaro Tanoi,[*,†,‡] Atsushi Hirose,[†] Takayuki Saito,[†] Akihiko Noda,[†] Naoko Iwata,[†] Akimasa Nakano,[§] Satoru Nakamura,[‖] and Tomoko M. Nakanishi[†]

[†]Graduate School of Agricultural and Life Sciences and [‡]Biotechnology Research Center, The University of Tokyo, 1-1-1 Yayoi, Bunkyo-ku, Tokyo 113-8657, Japan

[§]National Agriculture and Food Research Organization, 3-1-1 Kannondai, Tsukuba, Ibaraki 305-8517, Japan

[‖]Food Labeling Monitoring Department, Food and Agricultural Materials Inspection Center, 2-1-12 Kannondai, Tsukuba, Ibaraki 305-8642, Japan

Ⓢ *Supporting Information*

ABSTRACT: The mineral composition of taro (*Colocasia esculenta* (L.) Schott) was analyzed to develop a method to distinguish taro produced in Japan and China. The concentrations of 15 elements (Al, Ca, Cl, Mg, Mn, Br, Co, Cr, Cs, Fe, K, Na, Rb, Sc, Zn) were assayed using instrumental neutron activation analysis. The concentrations of NO_3^-, SO_4^{2-}, $H_2PO_4^-$, Cl^-, malate, and oxalate were measured by ion chromatography. The mean concentrations of $H_2PO_4^-$, Co, Cr, and Na significantly differed ($P < 0.01$) between taro grown in Japan and that grown in China. Discriminant analysis was performed to identify the most efficient combination of elements and compounds to discriminate the taro geographic origin. The highest percentage of correct classification was achieved with a two-variable model including $H_2PO_4^-$ and Co (100% for Japanese, 93.75% for Chinese). Principal component analysis and cluster analysis using all of the assayed elements and compounds were also conducted to determine which elements significantly accounted for the variation of the taro mineral composition. We report on the potential of $H_2PO_4^-$ and Co concentrations to differentiate taro grown in China and Japan and discuss the sources of variability in the taro mineral composition of our samples.

KEYWORDS: *Colocasia esculenta*, instrumental neutron activation analysis, mineral composition, cobalt, phosphate, principal component analysis, discriminant analysis

■ INTRODUCTION

Labeling of the geographic origin of food products is legally required in Japan to protect domestic producers of premium products and to protect consumers from overpayment. Despite this requirement, fraudulent labeling of geographic origin is frequently detected. Therefore, there is a continued interest in simple but robust methods to determine the geographic origin of both processed and fresh foods. To this end, several techniques have been developed involving the analysis of organic molecules,[1−4] mineral composition,[5−11] and isotope ratios.[12,13]

The purpose of this study was to analyze the mineral composition of taro (*Colocasia esculenta* (L.) Schott) grown in China and Japan. Taro is one of the major starchy food crops in Japan and has been cultivated for many years; a recent report published by the Ministry of Agriculture, Forestry, and Fisheries ranked the area under taro production as 12th among the major vegetables harvested in 2004. In recent years, both the production area and production volume of taro have gradually decreased, with a concomitant increase in the volume of taro imports. The overwhelming share of imported taro originated in China, especially in Shangdong province. The wholesale price of taro grown in China is approximately half that of taro produced in Japan, resulting in a substantial incentive to falsify the geographic origin of taro.

We analyzed the mineral composition of Chinese and Japanese taro to determine whether the mineral composition could

be used to discriminate the geographic origin. The mineral compositions of fruits, vegetables, and other edible plant parts are expected to reflect, at least partially, the mineral composition of the soil and environmental conditions in which the crops were grown.[8,14,15] Mineral composition analysis, which is one of the most widely used methods,[13] is a good candidate for distinguishing the geographic origin of taro. For mineral composition analysis we employed instrumental neutron activation analysis (INAA), which enables simultaneous, nondestructive analysis of a maximum of 45 elements. Three major elements, nitrogen, phosphorus, and sulfur, however, could not be analyzed by INAA due to low sensitivity and were analyzed using ion chromatography (IC).

Chemometrics, based on data for multiple elements, has frequently been used to determine geographic origin. These days, researchers can choose from a variety of multivariate techniques such as linear discriminant analysis, principal component analysis (PCA), or neural network classification to identify the most effective and robust method for determination of geographic origin. Such techniques have aided the development of methods to discriminate the geographic origin of a variety of
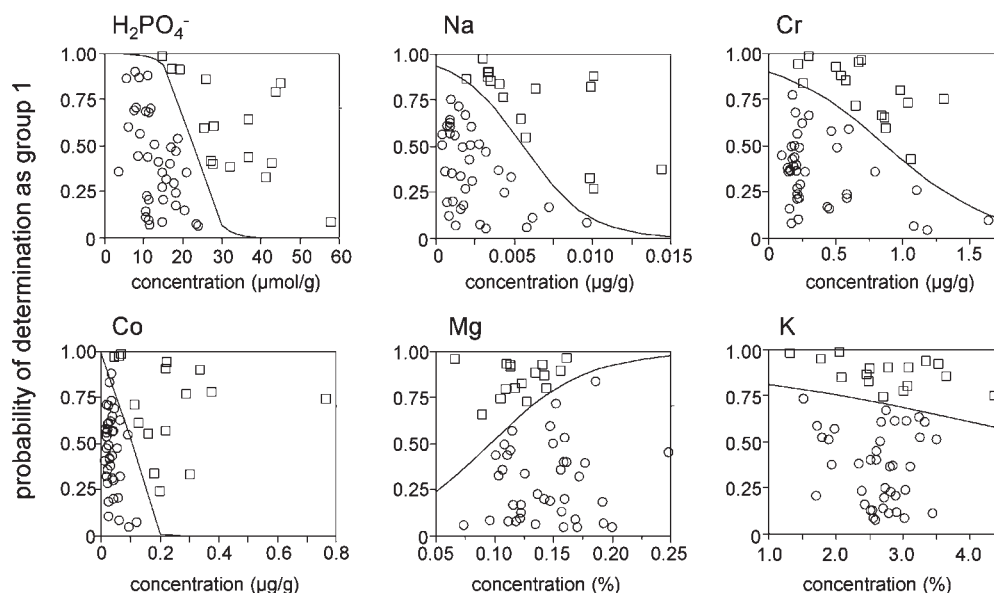
Figure 1. Diagrammatic representation of the logistic functions of $H_2PO_4^-$, Na, Cr, Co, Mg, and K for samples from group 1 ($\bigcirc$) and group 2 ($\square$). The sigmoidal logistic function curves of $H_2PO_4^-$, Na, Cr, and Co indicate that the concentrations of these elements and compound exceeded the threshold necessary for discriminating the groups.

crops with high probability. There is as yet, however, no single technique that can be considered a standard method for determining the geographic origin of crops. Only two elements, Ba and Sr, have been suggested as potential universal indicators of Japanese origin.[9] In this investigation, our approach was to use discriminant analysis to identify the smallest subset of elements that could be used to determine the geographic origin of taro, in anticipation of practical implementation of this method. In addition, we applied PCA to the entire set of measured elemental data to investigate factors affecting the mineral composition of taro.

■ MATERIALS AND METHODS

Sampling and Preparation. Fresh taro samples from Japan (group 1) were collected from wholesale suppliers, middle traders, and farmer's markets throughout Japan in 2008. A total of 39 samples were collected from 21 prefectures in Japan (Supplemental Table 2, Supporting Information). Chinese samples labeled as Chinese product (group 2) were collected from retail stores of Japan in 2008. All the samples were from different lots.

Samples were washed with water and peeled with a ceramic knife to avoid metal contamination. Samples were then smashed and homogenized. Each sample was freeze-dried and stored with dry silica at room temperature until analysis.

Instrumental Neutron Activation Analysis. In this study, 15 elements (Al, Ca, Cl, Mg, Mn, Br, Co, Cr, Cs, Fe, K, Na, Rb, Sc, Zn) were determined by INAA. Approximately 300 mg of freeze-dried sample was used for each INAA. Each sample was doubly sealed in an ultrapure polyethylene bag that was then placed in a polyethylene capsule. Thermal neutron irradiation was performed at the Japanese Research Reactor 3 (JRR3) of the Japan Atomic Energy Agency. Each capsule was irradiated for 30 s for short-term analyses or 20 min for long-term analyses. The thermal neutron flux for short-term analyses was 1.5×10^{17} m^{-2} s^{-1}, and that for long-term analyses was either 5.2×10^{17} or 4.7×10^{17} m^{-2} s^{-1} depending on the schedule regarding the operation of the nuclear reactor. A pure Ge counter (GX 1519, Canberra Inc., Connecticut) was used to measure the γ-rays emitted from the samples for 120 s for short-term analyses or for 60 or 500 min for long-term

analyses. The γ-ray energies used to determine each element are presented in Supplemental Table 1, Supporting Information. The standard materials (bush branches and leaves, NCS DC 73349, National Analysis Center for Iron & Steel, Beijing, China) were also irradiated to determine the element concentrations. Spectra obtained from short- and long-term analyses were analyzed with half-life correction using gamma studio software (Seiko EG&G, Tokyo, Japan).

Ion Chromatography. The concentrations of NO_3^-, SO_4^{2-}, $H_2PO_4^-$, and Cl^- were measured by IC. Additionally, malate and oxalate were also determined. A 1 mL volume of 0.1% Tween-20 reagent was added to 50 mg of the freeze-dried taro sample, which was then heated in a boiling water bath for 30 min. Samples were then centrifuged, and the supernatant was decanted and filtered. The supernatant solutions were diluted and passed through a Shodex IC NI-424 column (4.6 mm × 100 mm) and detected with a CD-5 conductivity detector (Showa Denko K. K., Tokyo, Japan). The detected ions were analyzed using ChromNAV software, version 1.12 (JASCO Co., Tokyo, Japan).

Statistical and Multivariate Analysis. The mean, standard deviation, and sample number for all elements and compounds were recorded for each sample group. Depending on the result of the F-test, either the Student's t test or Welch's t test procedure was used to identify variables (elements and compounds) whose means differed significantly by sample group. Nominal logistic regression analysis was also applied to check the potential of individual variables to discriminate geographic origin. Variables with logistic curves that exhibited the characteristic sigmoid shape were preferentially selected for discriminant analysis. To minimize the number of variables required for determination of geographic origin, which is essential for development of a rapid, practical method for field use, we calculated correlation ratios to measure the relative proportions of within-group and across-group dispersion. In addition, we performed forward stepwise selection, with the p-in value set at 0.05, to identify the most predictive variables to be used in the discriminant analysis. A discriminant function (DF) was then calculated using the selected subset of variables after converting the concentration to the Z-score. The software used in this study employed canonical discriminant analysis, whereby coefficients of the discriminant function were obtained on the basis of a method to maximize the correlation ratio. The concentrations of each element or compound were normalized so
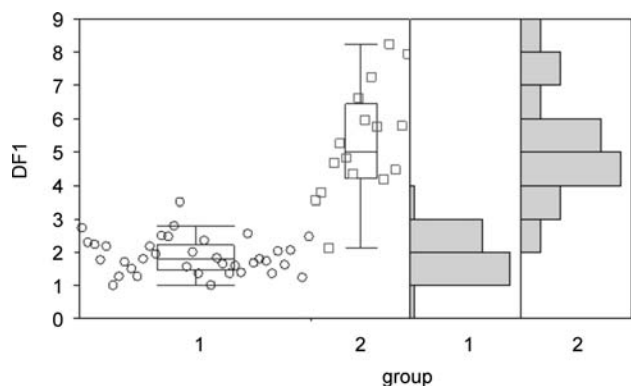
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Figure 2. Box-and-whisker and frequency distribution plots of discriminant scores obtained by DF1 for Japanese (○) and Chinese (□) taro samples.

that coefficients for each variable were comparable to facilitate evaluation of the contribution of each variable to determination of geographic origin. To check the contribution of each variable, we performed leave-one-out cross-validation (LOOCV) and confirmed the increase in misclassification rates due to omission of individual variables. PCA and cluster analysis were performed using log-transformed concentration data for the entire set of elements and compounds to identify new classifications regardless of geographic origin. Hierarchical clustering was performed using Ward's method. Statistical analysis was performed using JMP, version 6.0.3 (SAS Institute Inc.), and R 2.9.0 (http://www.r-project.org/) software.

■ RESULTS AND DISCUSSION

Mineral Composition Analysis. Concentration data for all elements and compounds measured in this study are presented in Supplemental Table 2, Supporting Information. The basic statistical analyses, including descriptive statics, F-test results, and p-values, are summarized in Supplemental Table 3, Supporting Information. Composition differences between sample groups were significant for Ca, Mg, Br, Sc, Zn, and oxalate at the $p < 0.05$ level and for Co, Cr, Na, and $H_2PO_4^-$ at the $p < 0.01$ level. Average concentrations of these latter four constituents were significantly higher in taro of Chinese origin than that of Japanese origin. Logistic graphs indicated that these four variables could be used to categorize the groups (Figure 1). Mg (significant difference in group means, $p < 0.05$) and K (no significant difference in group means) are examples of elements that could not be used to categorize groups (see Figure 1). Aluminum, Cs, and Sc were omitted from subsequent data analyses as so many samples appearing missing the value indicates that they have little potential to discriminate the geographic origin of taro.

Discriminant Analysis. Our first discriminant model was built using the variables (concentrations of $H_2PO_4^-$, Co, Cr, and Na, after conversion to the Z-score) which had a significant difference in group means at the $p < 0.01$ level and also showed the sigmoid-shaped logistic curve (Figure 1). Discriminant scores obtained by discriminant function 1 (DF1) indicated that the DF1 model was generally good in discriminating the geographic origin of taro (Figure 2). DF1 correctly classified all group 1 taro samples, but misclassified 2 of the 16 group 2 samples as group 1, resulting in a 12.5% misclassification rate for group 2 samples (Figure 2). We considered the following four points in developing a more accurate discriminant model. First, coefficients for the discriminant function for the four variables included in DF1

Table 1. Descriptive Statistics and Normalized Coefficients of the Discriminant Function for the Four-Variable ($H_2PO_4^-$, Co, Cr, and Na) Discriminant Model Based on DF1 and the Two-Variable ($H_2PO_4^-$ and Co) Model Based on DF2

	DF1	DF2
eigenvalue	2.51	2.39
Wilks' λ		
value	0.285	0.295
F-value	30.7	62.2
p-value	8.17×10^{-13}	1.62×10^{-14}
normalized coefficient of		
discriminant function		
$H_2PO_4^-$	1.14	1.23
Co	0.783	0.864
Cr	0.245	
Na	0.0943	

indicated that the concentrations of $H_2PO_4^-$ and Co were the most successful discriminators of geographic origin (DF1 column, Table 1). Second, evaluation of the correlation ratios (η^2), F-values, and p-values resulted in rejection of the null hypothesis ($\eta^2 = 0$) for all four variables, $H_2PO_4^-$, Co, Cr, and Na, at the 0.01 level (Table 2). Among the four variables, $H_2PO_4^-$ and Co exhibited the highest correlation ratios of 0.586 and 0.463, respectively. Third, $H_2PO_4^-$ and Co were also chosen by forward stepwise selection. Chromium was the third variable selected, but the p-value exceeded the p-in criterion of 0.05 (Table 3). Fourth, one sample in group 1 was misclassified as group 2 after LOOCV, indicating that DF1 overfits the data. On the basis of these four observations, Cr and Na were excluded from the second discriminant model.

In addition to the above points, reducing the number of variables in the discriminant analysis was also desirable to achieve the practical use of the developed discriminant model. The model based on discriminant function 2 (DF2), which included two variables ($H_2PO_4^-$ and Co), also successfully discriminated the geographic origin (Table 1). The DF2 model reduced the number of misclassifications over the DF1 model by one sample, resulting in misclassification rates of 0% and 6.25% for groups 1 and 2, respectively (Figure 3). In contrast to the DF1 model, misclassification rates for the DF2 model did not vary according to LOOCV, indicating that the model did not overfit the data.

The obtained discriminant model, DF2, misclassified one sample from group 2 as belonging to group 1 (Figure 3). To investigate the cause of this misclassification, we visually examined comparison circle plots representing group means for Co, Cr, Na, and $H_2PO_4^-$ (Figure 4). In all four cases, the pair of comparison circles do not intersect, indicating that means for group 1 and group 2 are significantly different (p-values are 0.00055 for Co, 0.0019 for Cr, 0.00084 for Na, and 0.0000068 for $H_2PO_4^-$; Supplemental Table 3, Supporting Information). The sample misclassified by both DF1 and DF2 models, indicated by the "×" in Figure 4, was plotted within the comparison circle for group 1 for all four variables. This is perhaps the reason why the sample was misclassified. In any case, this result suggests that, to achieve more accurate discrimination of the geographic origin of taro, it may be necessary to look beyond the elements or compounds analyzed in this study.

The sample misclassified in the DF1 model but not in the DF2 model (indicated by the solid square in Figure 4) was plotted closer to the comparison circle of group 1 than to that of group 2

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Table 2. Correlation Ratio (η^2), *F*-Value, and *p*-Value of 16 Elements and 5 Compounds to Taro Geographic Origin (Japan or China)

element	η^2	*F*-value	*p*-value
$H_2PO_4^-$	0.586	75.04	0.000
Co	0.463	45.67	0.000
Na	0.314	23.82	0.000
Cr	0.168	10.67	0.002
Mg	0.092	5.40	0.024
oxalate	0.074	4.25	0.044
Mn	0.053	2.97	0.091
Zn	0.044	2.41	0.126
Ca	0.040	2.22	0.142
Br	0.036	1.96	0.167
NO_3^-	0.022	1.20	0.278
Fe	0.014	0.74	0.395
SO_4^{2-}	0.014	0.73	0.397
Al	0.011	0.27	0.605
Rb	0.010	0.56	0.459
Sc	0.008	0.16	0.690
K	0.008	0.41	0.522
Cs	0.004	0.15	0.701
Cl^-	0.003	0.16	0.694
Cl	0.001	0.03	0.859
malate	0.000	0.00	0.998

Table 3. Results of Forward Stepwise Regression Analysis To Predict Taro Geographic Origin (Japan or China) Using 16 Elements and 5 Compounds[a]

	F-value	*p*-value
$H_2PO_4^-$	22.31	2.29×10^{-5}
Co	22.01	2.55×10^{-5}
Cr	2.647	0.111
SO_4^{2-}	2.141	0.150
Zn	2.067	0.158
Na	1.375	0.247
Mg	1.370	0.248
Ca	1.025	0.317
NO_3^-	0.5981	0.443
Mn	0.5235	0.473
Rb	0.5175	0.476
oxalate	0.3747	0.544
Fe	0.2513	0.619
malate	0.2215	0.640
K	0.1387	0.711
Br	0.06987	0.793
Cl^-	0.05573	0.814
Cl	0.03476	0.853

[a] Variables presented in order of inclusion in regression models.

in the cases of $H_2PO_4^-$, Cr, and Na, but not in the case of Co. Thus, the lower misclassification rate for the DF2 model was likely due to the increased coefficient of the discriminant function for Co (Table 1).
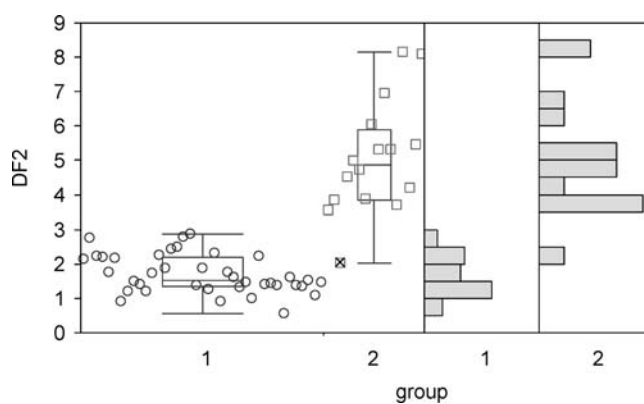
Figure 3. Box-and-whisker and frequency distribution plots of discriminant scores obtained by DF2 for Japanese (○) and Chinese (□) taro samples. One group 2 sample misclassified as group 1 is indicated by "×".

Principal Component Analysis. We performed PCA on 12 of the 16 elements measured and all 6 compounds measured. Seven samples were excluded from the analysis because they contained missing values for any elements or compounds (Supplemental Table 2, Supporting Information). The first principal component (PC1) and the second principal component (PC2) accounted for 40% of the total variability (Table 4). When the data were displayed with respect to the first three PCs, three clusters (clusters 1, 2, and 3) were apparent (Figure 5, Supplemental Table 2).

PC1 accounted for the maximum possible one-dimensional projection of the total variation of our data and was significantly influenced by Ca, Fe, and Zn (Table 4). Cluster 1, which was well separated from other clusters by the PC1 score, consisted of seven Japanese samples containing rather high concentrations of Ca, Fe, or Zn (Figure 5; Supplemental Table 2, Supporting Information). Since these samples were produced in six different prefectures, it is likely that the high concentrations of these elements are the result of excess fertilization, rather than a natural enrichment of these elements in the soil. PC2 was significantly influenced by $H_2PO_4^-$, Na, Cr, Co, and Mn, suggesting that PC2 responded to geographic origin (Table 4). The third principal component (PC3) was influenced by K, oxalate, and malate (Table 4). Considering that the organic acid contents in the potato tube were known to be changed during growth and storage,[16,17] PC3 may respond to the growth stage at harvesting time or the storage condition before selling. K could be the countercation of oxalate and malate, as the correlation values between K and oxalate/malate were especially high (0.82 and 0.84, respectively, data not shown).

Because information about the varieties of taro used in this investigation was scant, we could not determine whether clustering was due to differences in taro varieties. Nevertheless, on the basis of the fact that samples in group 1 identified as variety "Ishikawawase" were classified into both cluster 1 and cluster 2 (data not shown), clustering was unrelated to varietal differences at least for this variety. As a conclusion, cluster 1 could be characterized as the Japanese taro grown in the excess fertilization condition. Cluster 2 could be considered as the group of popular Japanese taro, and cluster 3 could be the popular Chinese taro group. For further precise characterization, additional experiments, such as the nutrient-dosage test and soil analysis, and information about the samples, including varieties and storage conditions, are needed.

Phosphorus, which is one of the major macronutrients in fertilizer, is primarily applied as phosphate. Because it is generally
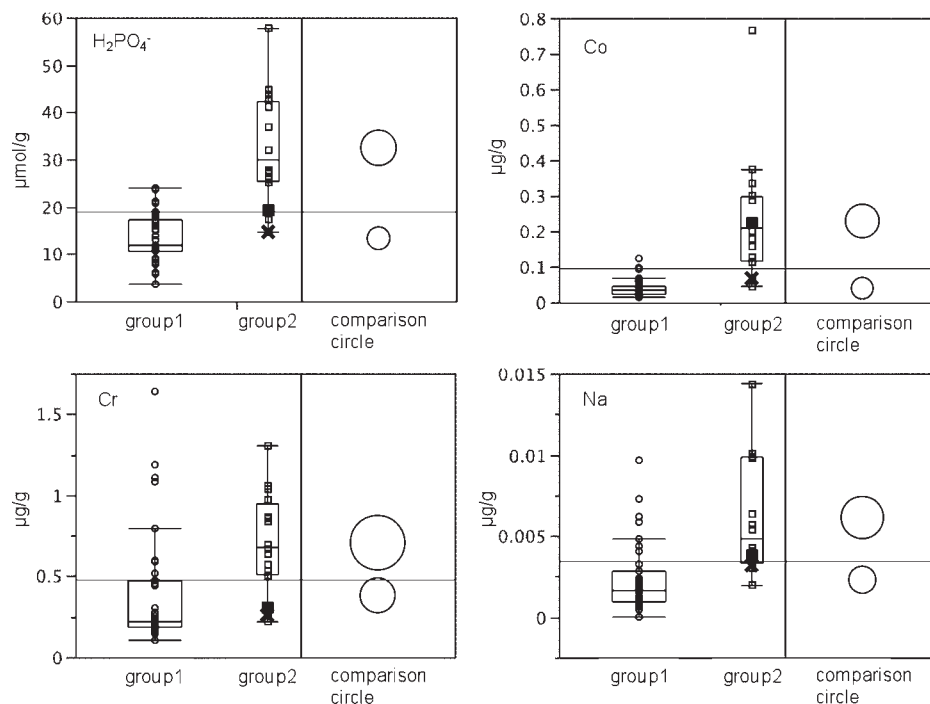
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Figure 4. Box-and-whisker plots and comparison circles by sample group for variables ($H_2PO_4^-$, Co, Cr, and Na) included in discriminant analysis models based on DF1 and DF2. The sample misclassified by the DF1 model is indicated by "■", and the sample misclassified by both DF1 and DF2 models is indicated by "×". The horizontal lines represent pooled mean concentrations for all the samples.

Table 4. First Three Principal Components for 13 Elements and 5 Compounds Measured in Taro

	PC1	PC2	PC3
Ca	0.390	−0.0830	0.0206
Fe	0.349	−0.0230	−0.0588
Zn	0.300	−0.00017	−0.0541
Co	−0.0563	0.474	−0.143
$H_2PO_4^-$	−0.0756	0.451	−0.154
Na	−0.0412	0.440	−0.0280
Cr	−0.0535	0.374	−0.0129
Mn	0.187	0.309	−0.104
K	−0.137	0.187	0.507
oxalate	−0.314	−0.0218	0.370
malate	−0.307	0.0993	0.337
Mg	0.0758	−0.103	0.291
Rb	−0.0622	−0.0365	−0.300
SO_4^{2-}	0.266	0.112	0.0265
NO_3^-	0.266	0.197	0.146
Br	0.245	−0.0384	0.262
Cl	0.278	0.127	0.295
Cl^-	0.296	0.0951	0.278
eigenvalue	4.31	2.97	2.35
contribution	23.96	16.48	13.07
cumulative	23.96	40.44	53.51

Figure 5. Principal component analysis (PCA) scores plot of PC1 vs. PC2. Using the first three PCs results in three sample clusters.

assumed that the concentration of $H_2PO_4^-$ in plants and soil is highly sensitive to artificial inputs, i.e., fertilizer, $H_2PO_4^-$ has not previously been analyzed as a potential indicator of geographic origin. However, Ariyama et al.[14] demonstrated that concentrations of soil-extractable P_2O_5 were not significantly correlated to
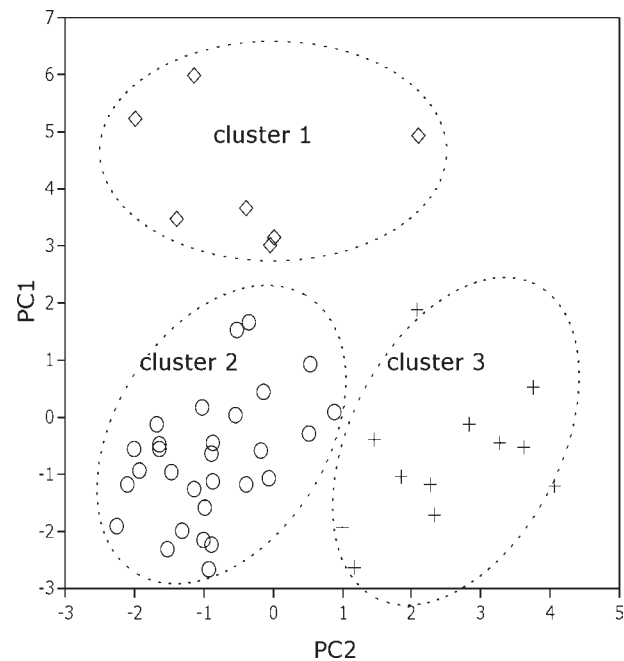
the concentration of P in onions, at least at the $p < 0.05$ level. Phosphate is easily captured and fixed by many soils, particularly Andisols, which are common in Japan. Therefore, the actual amount of P available to plants may not be correlated to the amount of P applied to a field as fertilizer. This notion is supported by the inverse relationship between the $H_2PO_4^-$ concentrations in taros produced in certain regions of Japan, such as Chiba, Miyazaki, Nara,

and Aichi Prefectures (Supplemental Table 2, Supporting Information) and the P_2O_5/N ratio of the fertilization standards for these regions (1.85, 1.15, 0.68, and 0.64, respectively, by mass) published by the Japanese Ministry of Agriculture, Forestry, and Fisheries (http://www.maff.go.jp/sehikijun/top.html; in Japanese). Thus, $H_2PO_4^-$ concentrations in taro may reflect the intrinsic P availability of the soil in which it was grown, rather than the magnitude of transient inputs in the form of fertilizer.

ASSOCIATED CONTENT

Ⓢ Supporting Information. Energy of the γ-ray peak for 15 elements determined by INAA (Supplemental Table 1) and the concentrations of elements and compounds of all samples (Supplemental Tables 2 and 3). This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author
*E-mail: uktanoi@mail.ecc.u-tokyo.ac.jp.

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