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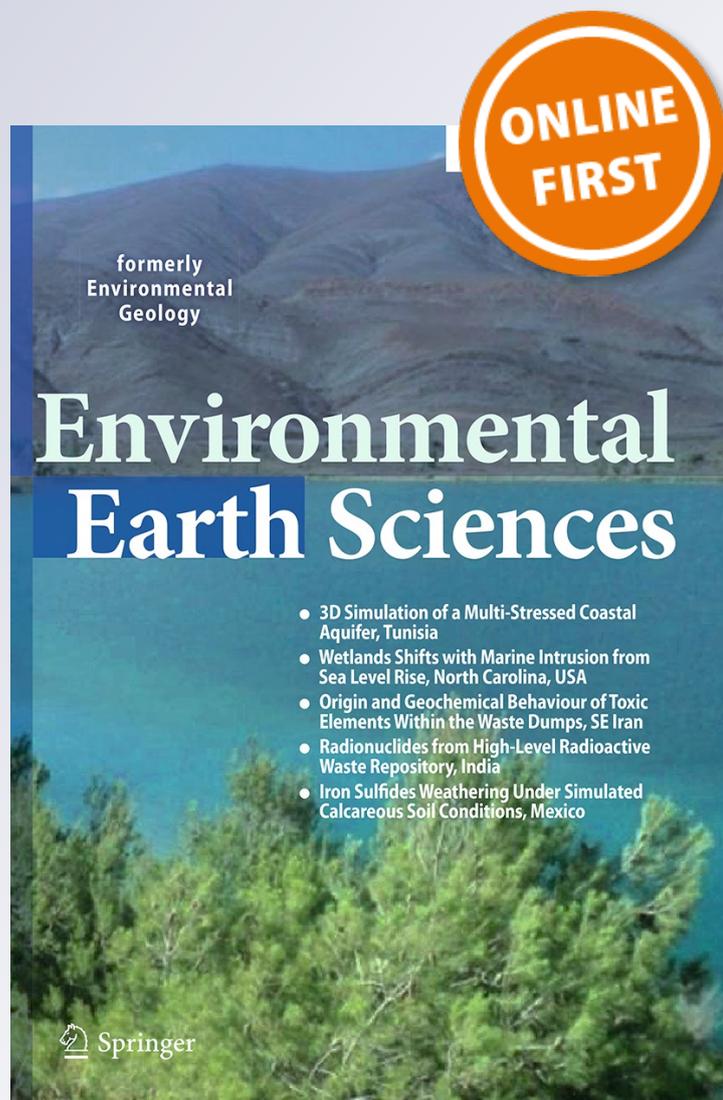
**Byeong-Yeol Song, Mukesh Kumar
Gautam, Jong-Sik Ryu, Dongho Lee &
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Environmental Earth Sciences

ISSN 1866-6280

Environ Earth Sci

DOI 10.1007/s12665-015-4087-2



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Effects of bedrock on the chemical and Sr isotopic compositions of plants

Byeong-Yeol Song · Mukesh Kumar Gautam ·
 Jong-Sik Ryu · Dongho Lee · Kwang-Sik Lee

Received: 22 June 2014 / Accepted: 21 January 2015
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Abstract This study was conducted to investigate the relationship between the chemical and isotopic compositions of plants and the lithology of their growth location. This relationship is one of the principles underlying the geographical discrimination used for agricultural, forestry, and food products. Locations in South Korea with solely basaltic (Jeju), granitic (Gongju), and carbonate (Yeongwol) rocks were selected as test sites, and bedrocks, soils, and plants in each location were sampled. The multi-element compositions and Sr isotope ratios ($^{87}\text{Sr}/^{86}\text{Sr}$) were analyzed for all samples, including various soil fractions (exchangeable, carbonates, silicates) and plant parts (tree leaves, vegetable leaves, and fruits). Based on a preliminary statistical analysis (ANOVA), Ca, Mg, K, Al, Sr concentrations, and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were selected as key variables with greater variability with location. Using these variables, a multivariate statistical analysis was conducted, and three soil fractions and plant

parts were successfully discriminated according to their geographical origin (i.e., bedrock type) with statistical significance. The results indicated that Sr isotope ratios of bedrocks can be preserved in soils (except in silicate fractions) and plants throughout weathering and plant physiological processes, and are the most critical variable in the tracing of bedrock characteristics.

Keywords Multi-element composition · Sr isotopes · Geographical discrimination · Multivariate statistical analysis

Introduction

The geochemical relationship between bedrocks and soils/plants is one of the principles underlying geographical discrimination studies. Plants take up vital components from soils that were originally derived from the weathering of basement rocks. During weathering, minerals in rocks are chemically and mechanically disintegrated, depending on their vulnerability, and their constituents are released into soils. The chemical composition of soils is primarily affected by the source rocks and the types of weathering processes. Therefore, the material cycles through the source rock–soil–plant system are the principle underlying the geographical discrimination used for agricultural, forestry, and food products, based on multi-element composition (Almeida and Vasconcelos 2003; Suzuki et al. 2008; Lo Feudo et al. 2010; Furia et al. 2011). For example, Almeida and Vasconcelos (2003) investigated the relationship between wines and their provenance soils using multi-element composition, and concluded that soil composition has potential for use as a fingerprint of the origin of wines.

Along with multi-elemental composition, stable isotopes have been increasingly used in studies of geographical

Electronic supplementary material The online version of this article (doi:10.1007/s12665-015-4087-2) contains supplementary material, which is available to authorized users.

B.-Y. Song · K.-S. Lee
 Graduate School of Analytical Science and Technology,
 Chungnam National University, Daejeon 305-764,
 Republic of Korea

B.-Y. Song · M. K. Gautam · J.-S. Ryu · D. Lee (✉) ·
 K.-S. Lee (✉)
 Division of Earth and Environmental Sciences, Korea Basic
 Science Institute, Chungbuk 363-883, Republic of Korea
 e-mail: dhlee17@kbsi.re.kr

K.-S. Lee
 e-mail: kslee@kbsi.re.kr

B.-Y. Song
 Chemical Analysis Division, National Forensic Service,
 Wonju 220-170, Republic of Korea

origin for plants and plant products because stable isotopes (such as carbon, oxygen, hydrogen, nitrogen, and sulfur) can be used to trace, record, and identify ecological parameters (Kelly et al. 2005; West et al. 2006; Rodrigues et al. 2011; Bong et al. 2012a; Rock 2012). For example, Rodrigues et al. (2011) used carbon, nitrogen, sulfur, and oxygen isotopes to identify the effects of varying climatic conditions on green coffee beans from the Hawaiian Islands. They suggested that stable isotope ratios can serve as a useful fingerprint to discriminate between different Hawaiian regions. Furthermore, radiogenic isotope ratios such as $^{87}\text{Sr}/^{86}\text{Sr}$ have been widely used in geographical discrimination studies. Radiogenic isotopes have an advantage over light stable isotopes in that they do not exhibit measurable fractionation during soil formation and plant physiological processes, so their ratios reflect only the geochemical characteristics of the rocks and soils from which they were derived (Degryse et al. 2010; Lee et al. 2011; Techer et al. 2011; Bong et al. 2012b). For example, Lee et al. (2011) examined the geographical origin of ginsengs grown in South Korea and China using $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, and concluded that their $^{87}\text{Sr}/^{86}\text{Sr}$ ratios reflect the lithological characteristics of the cultivation areas.

Previous studies have mainly focused on the practical application of geochemical variables to the tracing of geographical origin. However, few detailed analytical studies have been conducted on the geochemical relationship between bedrock–soil–plant systems, and the effects of various bedrock types and soil fractions. Soils are a complex mixture of components that can have different elemental and isotopic compositions (Opfergelt et al. 2014), so plants may uptake materials from selective soil fractions with elemental and isotopic compositions that differ from the bulk soils. The current study was motivated by the deficiency in knowledge about the geochemical relationships between bedrocks/soils and plants. We selected three study sites with different rock types (granite, basalt, carbonate) and collected samples of bedrocks, soils, and six plant species. We conducted multi-element and isotopic analyses of the samples including three soil fractions (exchangeable, carbonates, silicates) and plant parts (leaves and fruits). The objectives of this study were to elucidate the geochemical relationships between bedrocks, soils, and plant parts, and to identify the most suitable elemental and isotopic tracers for geographical discrimination studies.

Materials and methods

Samples

Three locations—Gongju, Yeongwol, and Jeju in South Korea—were selected for sample collection based on their

distinct lithology, including Mesozoic granites (Gongju), Paleozoic carbonates (Yeongwol), and Cenozoic basalts (Jeju; Fig. 1). In Gongju and Yeongwol, fresh rock samples were collected at the outcrops near the soil and plant sampling locations. Samples of basaltic rocks in Jeju were not collected in this study; geochemical data from previous studies were used instead (Chung and Land 1997; Shin et al. 1998; Choi et al. 2002; Yang et al. 2004; Tatsumi et al. 2005; Choi et al. 2006; Koh et al. 2008; Brenna et al. 2010, 2012). At each site, upper soils (0 ~ 5 cm) were collected from ~10 locations distributed over a 1-km² area with a total sample quantity ~0.5 kg dry soils. The six plant species, which were growing at all sampling sites, consisted of three tree species and three vegetable species: Acacia (*Acacia*), Zelkova (*Zelkova serrata*), Cherry (*Prunus serrulate* var.), Red pepper (*Capsicum annuum* L.), Corn/maize (*Zea mays* L.), and Spring onion (*Allium fistulosum* L.). For tree species, leaves ($N = 27$) were collected from the upper ($N = 9$), middle ($N = 9$), and lower parts ($N = 9$). For vegetable species, leaves ($N = 18$ samples) and fruits ($N = 13$) were collected (Table 1). Diverse sizes of vegetable leaves were collected to avoid possible size-dependent variability in the elemental and isotopic compositions. All plant samples were collected in triplicate.

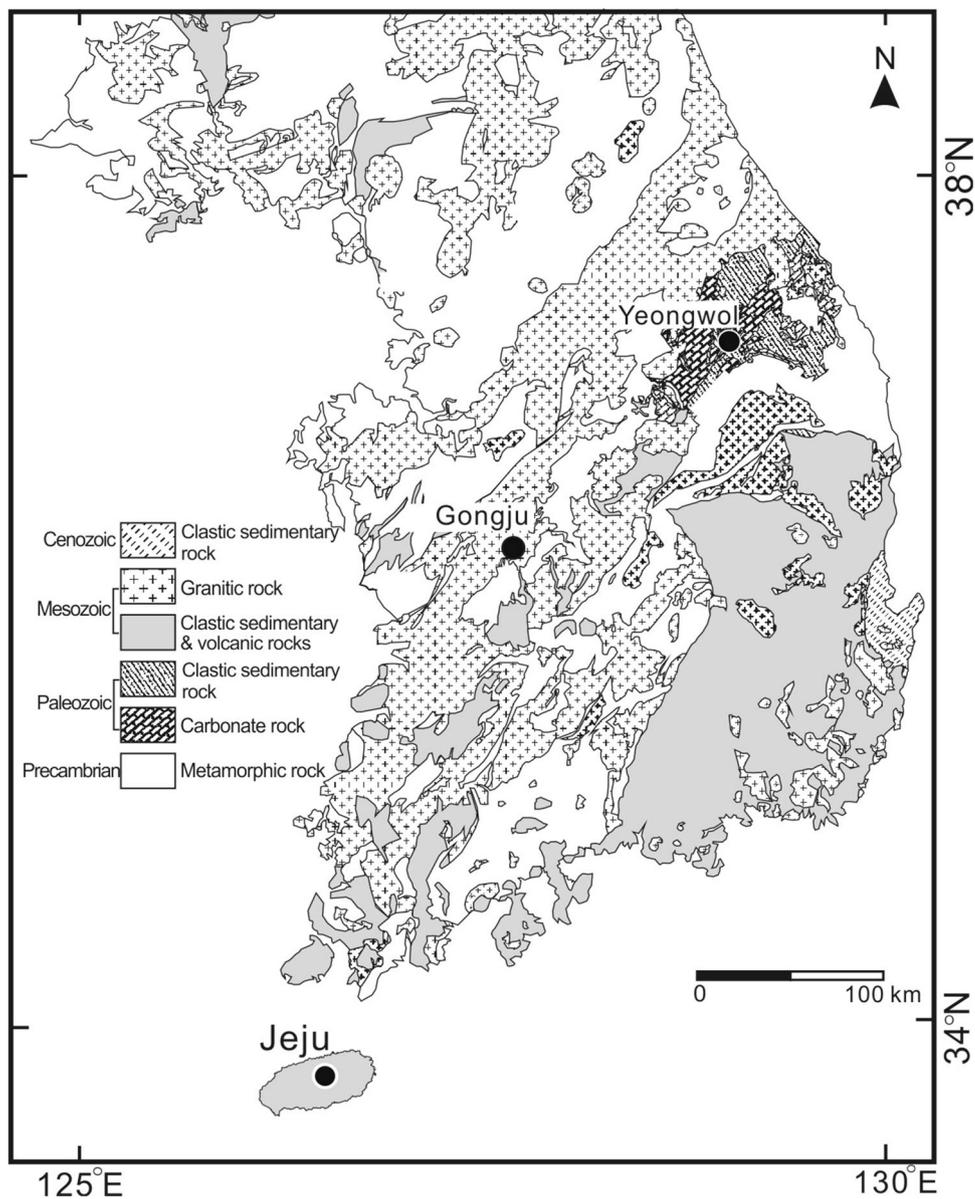
Sample preparation and analyses

Plants

To remove particles/dust from the surfaces of plant samples, samples were immersed in de-ionized water and repeatedly sonicated. After drying at 60 °C, the samples were ground using a medical mixer (HM-2500P, Medical Hyundai Inc., Korea) and kept in a vacuum oven. Approximately 0.7 g of powdered samples was digested in a Teflon vessel using 10 mL of 70 % HNO₃. After digestion, the solution was dried and residues were flushed several times by a 3:1 mixture of HNO₃ and HClO₄. This process was followed by re-dissolution in 3 % HNO₃ for the complete dissolution of samples.

Rocks and soils

Rock and soil samples were crushed by a shatter box equipped with tungsten carbide grinding jars. The crushed samples were wet sieved to smaller than 2 mm in diameter and for soil samples, particles larger than 2 mm in diameter were discarded. Crushed samples with diameters smaller than 2 mm were completely ground to powder. Approximately 0.1 g of each powdered soil and rock sample was completely digested in a 5:3 mixture of HF and HNO₃. Each sample was then dried, refluxed several

Fig. 1 Map of locations and lithologies of sampling sites

times by 6 M HCl to remove fluorides, and re-dissolved in 3 % HNO₃.

Sequential leaching of soils

A sequential dissolution method was used to extract exchangeable, carbonate, and residual (silicate) fractions of soils (Rauret 1998). Approximately 1 g of each soil sample was reacted with 10 mL of 1 M NH₄Ac for 6 h to extract the exchangeable fraction. After the reaction, the mixture was centrifuged and the supernatant was filtered using a 0.45- μ m polypropylene syringe filter. The filtered solution was dried and re-dissolved in 3 % HNO₃ to prepare for analysis. The residue of the previous step was reacted with

10 mL of 4 M HAc for 6 h to extract the carbonate fraction in soils, following the same procedure used to extract the exchangeable fractions. Finally, residue (mainly silicates) from the carbonate extraction step was dried at 60 °C and approximately 0.1 g of the subsample was completely digested in a 5:3 mixture of HF and HNO₃. Samples were dried and refluxed several times in 6 M HCl to remove fluorides, and then re-dissolved in 3 % HNO₃.

Multi-element analysis

Concentrations of major, minor, trace, and rare earth elements were determined using either ICP-OES (Optima 4300DV; PerkinElmer, Waltham, MA, USA) or ICP-MS

Table 1 Overview of the sampling locations and sample types

	Gongju	Yeongwol	Jeju
Coordinates	N127°15' 16"	N128°26' 4"	N126°33' 29"
	E36°21' 49"	E37°7' 22"	E33°25' 24"
Elevation (m)	118	192	71
Mean annual temp (°C)	12.3	10.7	16
Mean annual rainfall (mm)	1,354	1,200	1,872
Bedrock	Granite	Limestone	Basalt
	Mesozoic	Cambrian–Ordovician	Cenozoic–Paleocene
Samples types	<i>N</i>	<i>N</i>	<i>N</i>
Rock	1	2	–
Soil	5	11	6
Acacia leaves	3	3	3
Zelkova leaves	3	3	3
Cherry leaves	3	3	3
Red pepper	3	3	3
Pepper leaves	3	3	3
Corn	–	2	2
Spring onion	3	3	3

N number of samples analyzed

(X7, Thermo Scientific, Bremen, Germany) at the Korea Basic Science Institute (KBSI). Various standard reference materials (SRMs 1570a and 1573a for plants, SRMs BCR-2, G-3, and MAG-1 for soils and rocks) were used to verify the uncertainty involved in each analysis.

Strontium isotope analysis

Depending on the Sr concentration, approximately 0.2–1 mL of the sample solution was evaporated under laminar flow conditions and re-dissolved in 8 M HNO₃ to convert the matrix of the sample solution. Then, following the procedure described by Swoboda et al. (2008), Sr was separated from matrix elements using Eichrom Sr resin (Eichrom Industries, Darien, IL, USA). The eluted solution was evaporated and re-dissolved in 3 % HNO₃ to a final Sr concentration of ~200 ng/g. Sr isotopic ratios were measured using a double-focusing multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS) (Neptune, Thermo Scientific, Bremen, Germany) equipped with an CETAC autosampler (ASX-112FR). The analytical reproducibility of the measured ⁸⁷Sr/⁸⁶Sr ratios, based on a replicate analyses of NIST SRM 987, was 0.710247 ± 0.000008 (2σ, *N* = 24), with a negligible blank of less than 0.1 ng Sr.

Statistical analysis

As a first step, the chemometrics of rocks (25 elements), soils including different fractions (exchangeable-16

elements, carbonate-34 elements and silicate-47 elements), and plants (48 elements) were compiled and processed using a one-way ANOVA (Welch's ANOVA, SPSS Inc., Chicago, IL, USA). Based on these ANOVA results (*p* < 0.05), Ca, Mg, K, Al, Sr, and ⁸⁷Sr/⁸⁶Sr ratios were selected for further analysis due to their significant differences by location. Prior to the ANOVA, normality (Shapiro–Wilk's test) and homoscedasticity (Leven's test) were checked and normalized to log-values whenever *p* values were less than 0.05 (Zar 2010). Furthermore, a linear discriminant analysis (LDA) was conducted to test their efficiency in discriminating samples, based on their elemental and isotopic composition. Overall, the significance of the discriminant model was tested using Wilks' λ. In all the cases, Wilks' λ was highly significant (*p* < 0.0001), showing the relationship that there was statistically significant separation of the sites based on ⁸⁷Sr/⁸⁶Sr isotope ratios and all the elements selected. The Mahalanobis distance measure (*p* < 0.01) was used to support the results of the discriminant analysis. Tolerance values greater than 0.01 and VIF (Variance Inflation Factor) values less than 10 indicated the absence of multi-collinearity between variables. To determine the efficiency of discriminant analysis, cross validation procedure was used. Cross-validation through training and validation determines the percentage of observations correctly classified and determines to which group a particular observation belongs. We used default cross-validation mode in the XLStat for this wherein, 75 % observations were used in training samples and remaining 25 % observation in validation. All analyses

were performed using the XLStat-Pro[®] program (Addinsoft, New York).

Results and discussion

Multi-element concentrations

Bedrocks

Multi-element concentrations of all sample types are reported in the Appendix. For all locations, geochemical data reported in other studies were also used to calculate the average composition (Chung and Land 1997; Shin et al. 1998; Choi et al. 2002; Yang et al. 2004; Tatsumi et al. 2005; Choi et al. 2006; Koh et al. 2008; Brenna et al. 2010, 2012). Among the measured elemental concentrations, we focused on the five elements (Ca, K, Mg, Al, Sr) selected by the ANOVA, because of their suitability for geographical discrimination. In Fig. 2, concentrations of Ca and K in all sample types are shown as examples. In bedrock samples, Ca concentration varied with the abundance of Ca-bearing minerals such as calcium carbonates and Ca-rich plagioclases, i.e., the highest was in Yeongwol (carbonates), followed by Jeju (basalt), and the lowest was in Gongju (granite). As expected from the abundance of K-feldspars and micas, K concentrations were higher in Gongju than in other locations and lower in Yeongwol. Therefore, both Ca and K concentrations clearly differentiate locations with different bedrocks.

Soils

In bulk soil samples, Ca concentration was highest in Yeongwol, as with bedrock samples. However, the concentrations in Jeju and Gongju were similar (Fig. 2). The same pattern was observed for carbonate and silicate fractions. With regard to exchangeable fractions, Ca concentration was highest in Jeju with a large variability, and lowest in Gongju. Therefore, in soil and its fractions, Yeongwol can be identified from other locations based on its higher Ca concentration, except in exchangeable fractions.

K concentration markedly varied by location in soil and its fractions, although the pattern of variability differed from that of bedrock (Fig. 2). In bulk soils and silicate fractions, K concentrations were lower in Jeju and higher in Gongju and Yeongwol. In exchangeable and carbonate fractions, the variability in K concentration exhibited a reversed pattern compared with that of bedrocks, that is, it was highest in Yeongwol, intermediate in Jeju, and lowest in Gongju. In summary, although the variability in the elemental concentrations of soil and its fractions may not

strictly follow the pattern observed in bedrocks, Ca and K (and also Mg, Al, Sr) concentrations varied with location, supporting the utility of these elements for the tracing of geographical origin.

Plants

The variability in Ca concentrations of tree and vegetable leaves was similar to that observed in the bulk soils, carbonate, and silicate soil fractions, although with less difference in concentration by location (Fig. 2). Differences in concentration were most remarkable in vegetable fruits, which had the highest Ca concentrations in Gongju and the lowest in Jeju. K concentrations were higher in Gongju and lower in Jeju, with considerable variability. Differences in K concentration by location were small or negligible in tree and vegetable leaves.

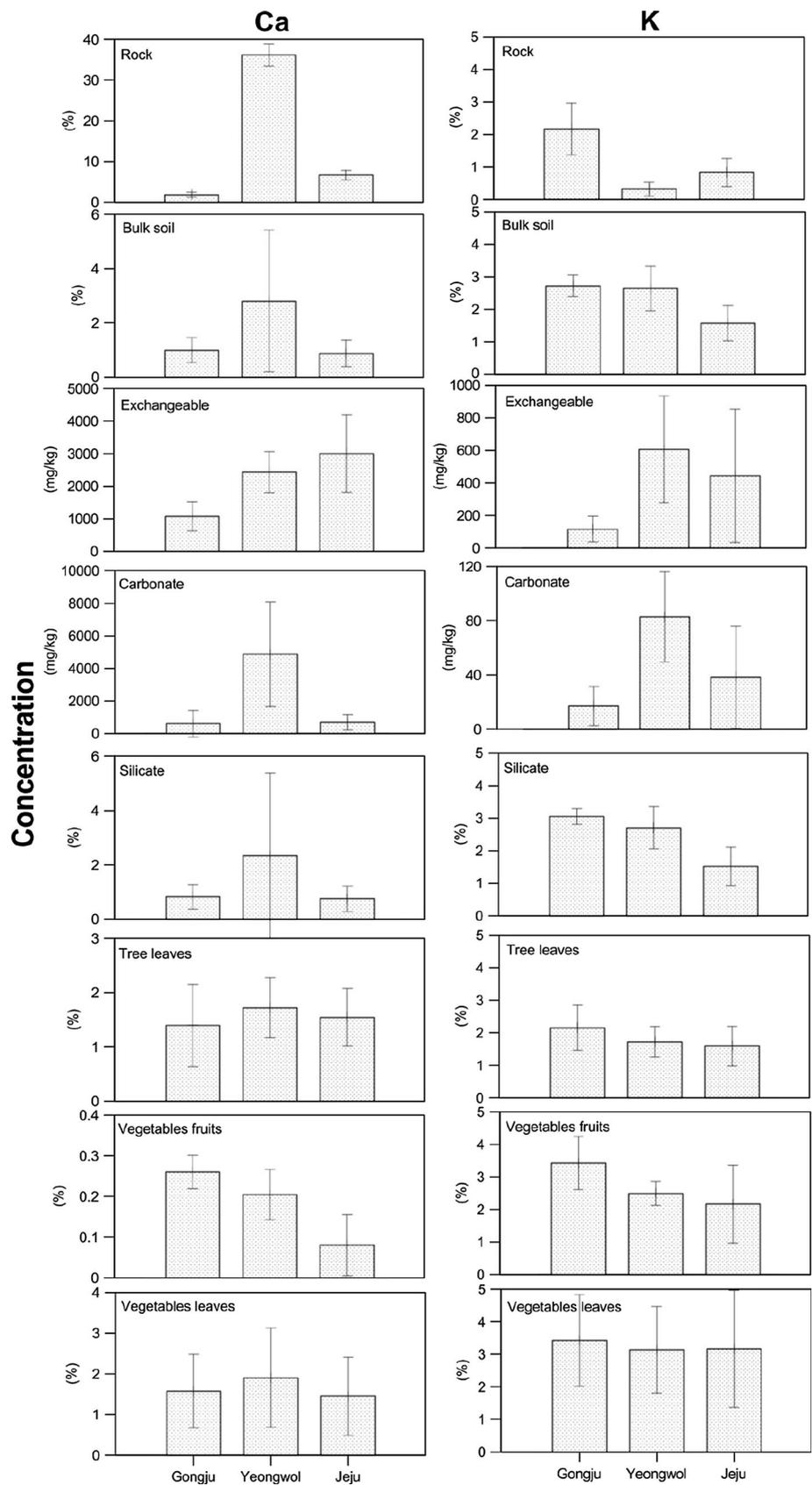
The effectiveness of using elemental concentrations to trace plant origins may vary by elements and plant parts, as discussed previously. In many cases, the elemental concentrations of plants varied sufficiently by location, but this variability did not strictly follow the pattern observed in bedrocks or in specific soil fractions. The complexity in plant elemental concentration may be related to the plant physiological processes and the compositional difference in various soil fractions. Some previous studies have suggested that plants may uptake essential elements for nutrition from the exchangeable fraction of soils. However, based on our results, it is difficult to relate plant elemental composition to specific soil fractions. Nevertheless, the findings suggest that large compositional differences in bedrocks can be inherited to plant elemental composition in various and unspecified ways, thereby enabling the identification of geographical origin.

Strontium isotope ratios

Bedrocks

The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were highest in Gongju and lowest in Jeju (Fig. 3). This finding is consistent with the reported $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for similar rock types collected in Korea: 0.70402–0.70623 for Cenozoic sedimentary and volcanic rocks (Kim et al. 1999a, 2003); 0.71067–0.75594 for Mesozoic granites (Cheong and Chang 1997; Kwon et al. 2006); and 0.70916–0.715573 for Paleozoic carbonate rocks (Chung and Land 1997; Park and Cheong 1998; Kim et al. 1999b). The radiogenic signature of carbonate rocks compared with Phanerozoic marine carbonates can be explained by the dissolution of metamorphosed carbonates such as marbles (Park and Cheong 1998). The wider variation in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of bedrocks in Jeju may be related to the fact that we compiled previously reported

Fig. 2 Concentrations of Ca and K in bedrocks, bulk soils, soil fractions, and plant parts



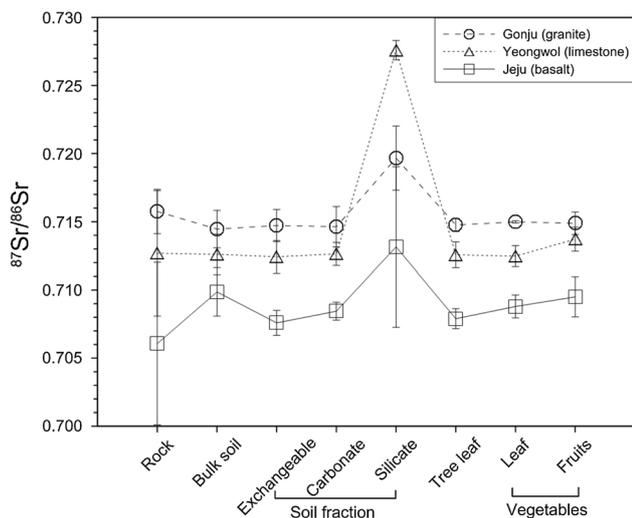


Fig. 3 $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of bedrocks, bulk soils, soil fractions, and plant parts

data and did not conduct our own analyses of bedrock samples.

Soils

The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of bulk soils were similar to those of bedrocks in Yeongwol, slightly lower in Gongju and higher in Jeju (Fig. 3). In Jeju, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of exchangeable and carbonate fractions were lower than those of the bulk soils, while in other locations, the ratios of bulk soil, exchangeable, and carbonate fractions were almost constant. The silicate fractions of soils had exceptionally higher ratios in all locations, which was most remarkable in Yeongwol with its carbonate bedrocks. In terms of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, it is clear that the silicate fractions cannot accurately represent the bedrock characteristics.

Plants

In Gongju, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of all plant parts were similar to those in the bulk soils and soil fractions except for silicates (Fig. 3). In Yeongwol, although the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of fruits were slightly higher, the ratios of other plant parts were almost identical to those of bedrocks, bulk soils, and soil fractions (except silicates). In Jeju, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of plant parts were in the range of the ratios measured for bulk soils, exchangeable soils, and carbonate fractions.

Overall, the distinct $^{87}\text{Sr}/^{86}\text{Sr}$ ratio at each sampling location was maintained in soils and plant parts except in the silicate fractions. The results indicate a remarkable consistency of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios throughout the bedrock–soil–plant pathway, which substantiates the utility of Sr isotopes in geographical discrimination studies. No matter which plant part is used, the geographical origin can be

effectively traced based on the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio alone, given that they were cultivated in regions with different Sr isotope ratios.

Geographical discrimination

Discriminant analysis using Ca, Mg, K, Al, Sr concentrations and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios as descriptors revealed that all locations, and the plants growing there, had significantly different chemical compositions ($p < 0.05$, see Fig. 4). Elemental patterns of plants' leaves were well distinguished by locality. The probability of successful classification was also very high in all cases: 100 % for plants and rocks, 93.3 % for exchangeable and carbonates fractions, 73.3 % for silicate fractions. Furthermore, the significant Mahalanobis distances ($p < 0.01$), which were calculated with all pairwise distances between sites for all treatments, differed significantly regardless of which fraction was used (Fig. 4). For all cases, the first two discriminant functions differed significantly between the locations ($p < 0.0001$; Table 2). Because canonical correlation measures the strength of the overall relationships between the linear canonical discriminant functions and descriptor variables, a highly significant canonical correlation between the locations and the first/second discriminant functions ($p < 0.05$) indicates that the canonical functions can explain the differentiation of the locations. Use of discriminant analysis successfully classified plants' leaves relative to their distributed grown area. This finding indicates that the chemistry of plant leaves reflects their habitat environment, i.e., mainly bedrock lithologies.

Conclusions

The significant differences in bedrock composition [granite (Gongju), carbonate (Yeongwol), and basalt (Jeju)] apparently influenced the composition of the weathering products (soil and its fractions) and plants cultivated from the region. Concentrations of Ca, K, Mg, Al, Sr, and Sr isotope ratios exhibited the most variability by the locations of different bedrocks. In particular, Sr isotope ratios of bedrocks were maintained in soils (except in the silicate fractions) and plants, and therefore can be used as an unequivocal tracer to identify a plant's geographical origin. Use of discriminant analysis based on Ca, Mg, K, Al, Sr, and Sr isotopes successfully classified plants according to their growth locations, based on the bedrocks and soils. Our results demonstrate that carefully selected geochemical variables can identify plant habitat information with the help of statistical analysis techniques. Although here we suggested Ca, Mg, K, Al, Sr, and Sr isotopes as key variables for geographical discrimination for use in geological

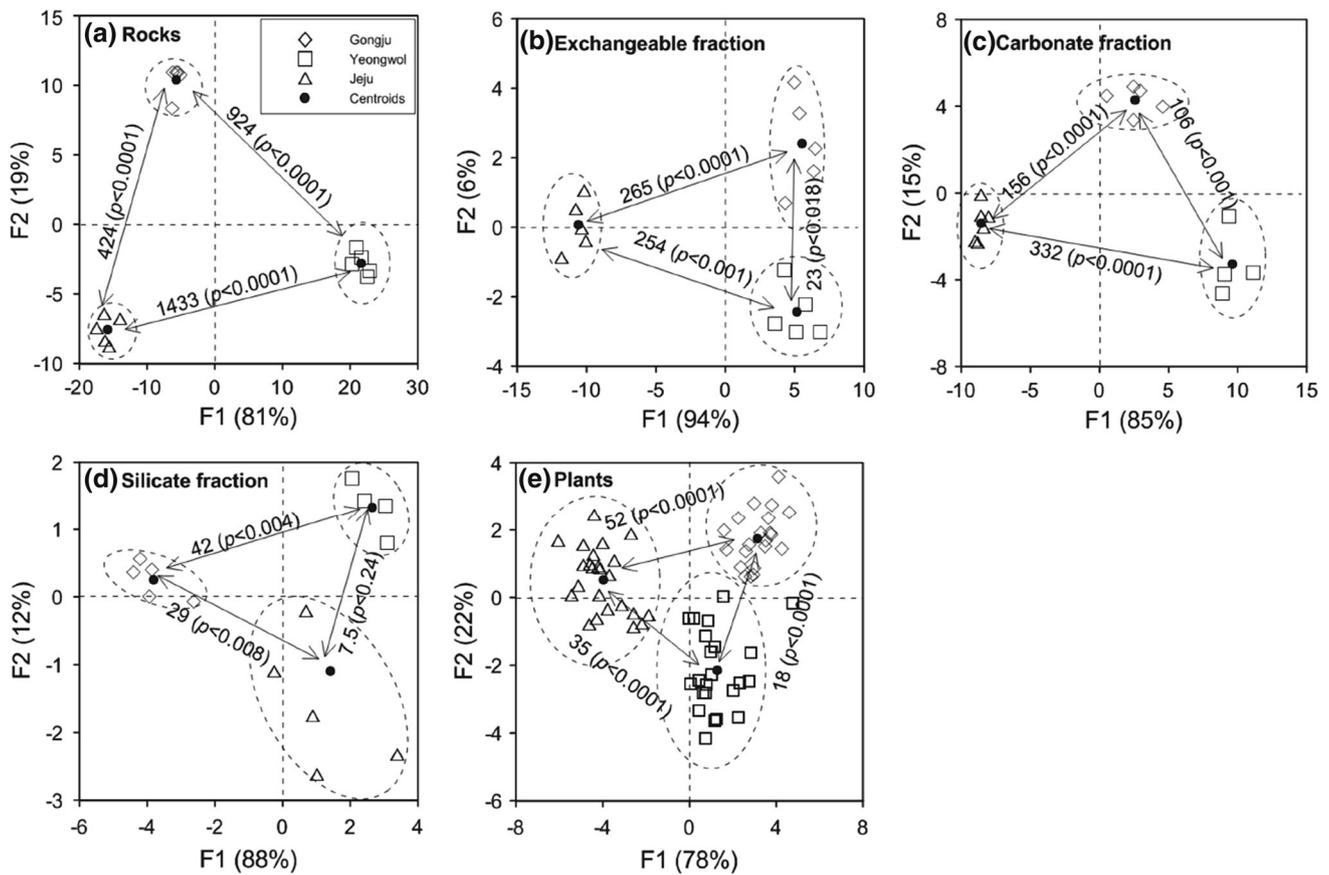


Fig. 4 Scatter plots of linear discrimination analysis for rocks, soils including exchangeable, carbonate, and silicate fractions, and various plant parts with the Mahalanobis distance

Table 2 Results of linear discriminant analysis for all the samples

	Plants		Rock		Exchangeable fraction		Carbonate fraction		Silicate fraction		Three fractions + rock	
	F1	F2	F1	F2	F1	F2	F1	F2	F1	F2	F1	F2
Eigenvalue	48.4	5.5	315	71.9	70.6	4.9	70.1	12.3	9.4	1.2	576	132
Discrimination (%)	78	22	81	19	94	7	85	15	88	12	77	18
Cumulative (%)	90	100	81	100	94	100	85	100	88	100	77	95
Canonical correlations	0.99	0.92	1	0.99	0.99	0.91	0.99	0.96	0.95	0.74	1	1
<i>Coefficients of standardized canonical discriminant function</i>												
⁸⁷ Sr/ ⁸⁶ Sr	7.8	0.0	0.2	0.7	2.2	0.2	1.9	0.9	0.9	0.6	0.0	0.0
Al	-0.7	1.4	-1.7	-0.8	-0.9	0.1	-0.1	-0.2	-1.0	0.2	1.5	-0.3
Ca	2.7	-1.4	0.6	-0.1	2.6	-0.2	6.2	-0.2	-1.1	-0.3	0.1	1.0
K	-1.3	2.6	0.2	1.7	0.2	-0.4	2.2	-1.3	-1.2	0.4	0.6	0.4
Mg	0.4	-3.0	-1.7	0.6	-1.0	-0.8	-4.7	-0.9	1.4	0.2	1.9	-0.2
Sr	-1.1	1.7	-0.4	0.0	-1.1	0.9	-2.6	1.8	1.1	0.2	0.5	0.1

settings, future research may reveal more geochemical proxies and extend the applicability to more diverse rock types.

Acknowledgments This study was supported by a national agenda program (NAP) of the Korea Research Council of Fundamental Science & Technology and by a KBSI grant (C34701).

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