Determination of the Geographic Origin of Brown-Rice with Isotope Ratios of ^{11}B/^{10}B and ^{87}Sr/^{86}Sr

Hisao ODA[1†], Akira KAWASAKI[1] and Takafumi HIRATA[2]

[1†] *National Institute for Agro-Environmental Sciences, 3-1-3 Kannondai, Tsukuba, Ibaraki 305-8604, Japan (E-mail: odah@niaes. affrc.go.jp)*

[2] *Laboratory for Planetary Sciences, Tokyo Institute of Technology, O-okayama 2-12-1, Meguro, Tokyo152-8551, Japan*

This study was conducted to identify of the geographical origin of brown-rice samples (*Oryza sativa* L.) by means of the binary isotope signature of ^{11}B/^{10}B and ^{87}Sr/^{86}Sr. Rice samples were collected from 44 different locations in Japan, 4 in China, 3 in Australia, and 1 each in Vietnam and California. The results of this study indicate that ^{11}B/^{10}B and ^{87}Sr/^{86}Sr ratios could distinguish rice samples yielded in Japan (^{11}B/^{10}B:3.97-4.13 and ^{87}Sr/^{86}Sr:0.706-0.709) from samples yielded in Australia (^{11}B/^{10}B: 4.10 and ^{87}Sr/^{86}Sr: 0.714), samples yielded in China and Vietnam (^{11}B/^{10}B:4.02-4.05 and ^{87}Sr/^{86}Sr:0.710-0.711), and samples yielded in California (^{11}B/^{10}B:4.09 and ^{87}Sr/^{86}Sr:0.706). Analytical method: The two solutions were digested by dry ashing (ca. 5-10 g sample) and microwave-assisted acid digestion (ca. 0.2 g sample). ^{11}B/^{10}B ratios in the digested sample solution were determined by ICP-QMS after purification by the ion exchange method (IRA743). The ^{87}Sr/^{86}Sr ratio was determined by Multiple Collector-ICP-MS after removal of rubidium from the acid digested solution by means of the ion exchange method (Dowex 50w X8). The intensities of ^{86}Sr and ^{87}Sr were corrected from the intensities of ^{83}Kr and ^{85}Rb. The precision of relative standard deviation (%) (Mean ± SD, [n]) of the ^{11}B/^{10}B and ^{87}Sr/^{86}Sr determination in the rice samples were 0.203 ± 0.073, [34] for the dry ashing method, 0.369 ± 0.142, [10] for the microwave-assisted digestion method, and 0.056 ± 0.028, [43] for ^{87}Sr/^{86}Sr.

In Japan, agricultural products must be sold with the place of harvest and the variety of the product displayed on the label. The prices of agricultural products including rice vary according to the production area, with rice produced in certain areas selling at higher prices. So far, no reliable method has been established to determine the area of origin of agricultural products. As a result it is possible that there are many cases of false labeling, particularly in the famous Japonica-rice brand.

The determination of the origin of agricultural products, by means of element composition signature in brown-rice,[1] polished-rice,[2] tea,[3] potato,[4] and wine,[5] has been reported. Yasui and Shindoh [1] showed that it is possible to identify the production area of rice through the analysis of microelement composition in rice. Kawasaki and Oda,[6] demonstrated a significant difference in the boron isotope ratio (B-IR: ^{11}B/^{10}B ratio) between Australian and Japanese rice. Microelement composition and B-IR of rice can be used as a key to infer the rice provenance, but more information is needed for precise identification. The determination of the provenance of agricultural products by element composition signature is less reliable than that by the isotope signature. This is because the element composition of rice vary not only according to the place of harvest, but also according the variety,[1] and polishing rates.[7] Moreover, the cadmium concentrations in rice grains also vary according to the positions of the grain in an ear.[8]   Recently, wine provenance has been

successfully determined by using Sr isotope signatures.[9, 10] It has also been reported that ^{87}Sr/^{86}Sr ratios (Sr-IR) of plant roots are close to soil ratios,[11] and that the soil solution and the plant have the same Sr-IR ratio,[12] indicating that these ratios are not affected by fractionation due to geological and biological processes.[13]

In this study, B and Sr were chosen as the isotope elements, since ICP-MS has a very high sensitivity for element determination that it is possible to precisely determine the provenance of the brown-rice samples, containing as little as a few mg to less than a mg kg^{-1} of B and Sr, and because the anthropogenic contamination can be disregarded due to the low content of both elements in farm chemicals such as fertilizers for paddy field. In addition, geochemical studies for exploring resources, assumes that the isotope ratio (IR) reflects the characteristic information in water from B[6, 14, 15] and the chronological information in parent material from Sr[16] of the provenance.

Experimental

Materials

Domestic brown-rice, main variety of Koshihikari collected from 44 locations in Japan and foreign brown-rice, 4 in China, 3 in Australia, and 1 each in Vietnam and California. were investigated.

Methods
Procedure for B-IR Determination. Determination of B-IR in brown-rice was carried out following the procedure described in a previous study.[6] This method consisting of three parts, i.e., (1) two different sample digestion procedures, (2) the B separation procedure shown in Fig. 1, and (3) the B determination by ICP-MS (SPQ 8000A, Seiko Instruments Inc., Japan).
Accuracy and Precision of B-IR Determination. SRM951 as a standard sample for B-IR determination was 4.05 ± 0.01 on average at 10 μB was within 1σ standard deviation of the certified value ($^{11}B/^{10}B=4.04362 \pm 0.00137$). The precisions of relative standard deviation(%) (Mean± SD[n]) of the $^{11}B/^{10}B$ determination in the rice samples were $0.203 \pm 0.073[34]$ for the dry ashing and $0.369 \pm 0.142[10]$ for the microwave-assisted digestion.
Procedure for Sr-IR Determination. Determination of Sr-IR in brown-rice was done according to the method reported by Kawasaki and Oda.[17] This procedure consisted of three parts, i.e., (1) the acid digestion procedure, (2) Sr separation as shown in Fig. 2, and (3) Sr determination by the the multiple collector-

(MC)-ICP-MS (Plasma54, VG Elemental Co., UK). The strontium concentration in the digested sample solution was determined by the method reported by Kawasaki *et al.*[18]
Accuracy and Precision of Sr-IR Determination. Six different mass numbers were measured (^{83}Kr, ^{84}Sr, ^{85}Rb, ^{86}Sr, ^{87}Sr and ^{88}Sr). The intensity of ^{87}Sr was corrected using that of ^{87}Rb, which was calculated from that of ^{85}Rb. The Sr-IR was corrected by the mass bias factor calculated from the measured value of $^{86}Sr/^{88}Sr$ ratio.

The result measuring Sr-IR ($^{87}Sr/^{86}Sr$) of the standard sample (SRM987) at 0.2 mg Sr L^{-1} is shown in Table 1. The measured value of the Sr-IR of SRM987 was within 0.71020-0.71027, which coincided with the accepted value of 0.710248 up to 4 figures. The precisions of relative standard deviation (%) (Mean ± SD, [n]) of $^{87}Sr/^{86}Sr$ in 43 rice samples were 0.056 ± 0.028 [43].

Table 1   Analysis of NIST SRM 987, 200ppb

No	$^{87}Sr/^{86}Sr$	SD[1]	RSD[2] (%)	Accuracy[3] (%)	n
1	0.71027	0.00012	0.017	0.0026	57
2	0.71020	0.00013	0.018	-0.0065	58
3	0.71025	0.00010	0.014	0.0006	58
4	0.71027	0.00015	0.021	0.0031	56
5	0.71027	0.00018	0.025	0.0033	58
6	0.71022	0.00024	0.034	-0.0041	59

1) Standard deviation.
2) Relative standard deviation.
3) Percent deviation from the accepted value (0.710248).

Results and Discussion

Concentration and B-IR in Brown-Rice. The B concentrations and $^{11}B/^{10}B$ ratios in the brown-rice samples ranged from 0.33-1.26 mg kg^{-1} and from 3.97-4.19, respectively. The B concentration of Japanese and the foreign-grown rice ranged from 0.33-1.26 mg kg^{-1} and from 0.54-1.13 mg kg^{-1} respectively, indicating a similar range in domestic and foreign-grown rice. Therefore Japanese and foreign-grown rice could not be discriminated using the B concentration. In the case of the 44 samples of Japanese rice, the $^{11}B/^{10}B$ ratios ranged from 3.97-4.13, and about 3/4 of them ranged from 4.01-4.06. Australian rice had the highest $^{11}B/^{10}B$ ratio (4.14-4.19) among all rice samples examined. Californian rice had a higher IR (4.09) than almost all Japanese rice samples. The IR of Chinese and Vietnamese rice (4.02-4.05) was similar to that of domestic rice.

These results indicated that the identification of the rice production area in Japan is difficult since the distribution range of B-IRs were too narrow to discriminate by means of the B isotope signature. Furthermore, there is insufficient geological information with respect to B-IR distribution. It is however clear that foreign-grown rice, especially Australian rice, can be identified from the B-IR samples, Australian rice had the highest $^{11}B/^{10}B$ ratio(4.14-4.19) among all rice samples examined. It might reflect the high B-IR in surface brackish and freshwaters in Australia.[19]
Concentration and Sr-IR in Brown-Rice. The Sr concentrations of Japanese and foreign-grown rice ranged from 0.11-0.45 mg kg^{-1} and from 0.15-0.51 mg kg^{-1} respectively, indicating a similar range in domestic and foreign-grown rice. Therefore Japanese and foreign-grown rice could not be discriminated using the Sr concentration. In the case of 34 samples of Japanese rice, the IRs ranged from 0.706-0.709, with a mean of 0.708. Within the foreign-grown rice, the $^{87}Sr/^{86}Sr$ of Chinese and Vietnamese rice, and Australian rice had a range of 0.715-0.717 and 0.710-0.711 respectively, and were higher than those of domestic rice; therefore it was possible to discriminate them from Japanese rice. The reason that Sr-IRs of China and Vietnamese rice were higher than those of domestic can be attributed to the effect of aeolian
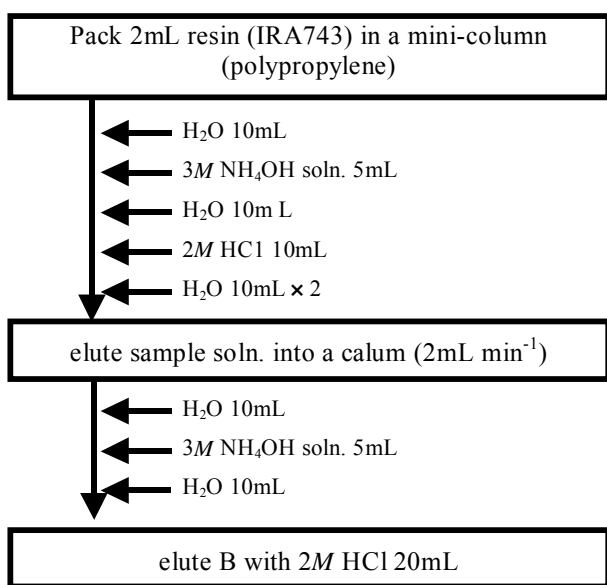

Fig. 1 Boron separation by means of the ion-exchange resin, Amberlite IRA-743.
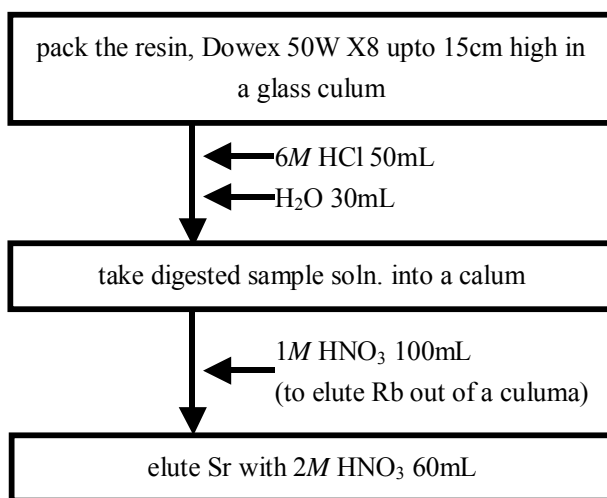
Pack 2mL resin (IRA743) in a mini-column (polypropylene)

→ H_2O 10mL
→ 3M NH_4OH soln. 5mL
→ H_2O 10m L
→ 2M HCl 10mL
→ H_2O 10mL× 2

elute sample soln. into a calum (2mL min^{-1})

→ H_2O 10mL
→ 3M NH_4OH soln. 5mL
→ H_2O 10mL

elute B with 2M HCl 20mL

Fig. 2 Strontium separation from rubidium by means of the ion-exchange resin, Dowex 50W X8.

pack the resin, Dowex 50W X8 upto 15cm high in a glass culum

→ 6M HCl 50mL
→ H_2O 30mL

take digested sample soln. into a calum

→ 1M HNO_3 100mL (to elute Rb out of a culuma)

elute Sr with 2M HNO_3 60mL

dust (^{87}Sr/^{86}Sr=0.719) originating in the Asian continent. Aeolian dust decreases close to Izu and Ogasawara-Mariana island arc (^{87}Sr/^{86}Sr=0.703-0.705).[20] The Sr-IR of Californian rice was 0.706. In California, Sr-IRs of rocks was a range of 0.703-0.708, were lower than 0.706 over a large region of seaside,[21] which range may reflect the analytical value of Californian rice. Therefore, Californian rice could also be discriminated from Japanese rice, since the value of California was lower than that of domestic rice.

Analysis by the Binary Isotope Signature of B and Sr in Brown-Rice
For whole samples. Figure 3, shows a scatter plot of binary IRs of B and Sr in the whole brown-rice samples. Australian rice group with the highest IRs of B and Sr was plotted over in Fig. 3, and it is clear that IRs of B of Australian rice is isolated from the plots of the other countries. Data from Chinese and Vietnamese rice with higher ^{87}Sr/^{86}Sr ratios than domestic rice was also plotted over data from domestic rice. Compared to domestic rice, in the single sample of Californian rice that was analyzed, the ^{11}B/^{10}B ratio was higher and the ^{87}Sr/^{86}Sr ratio was close to the lowest value (0.706) of domestic rice. Thus, it is clear that by the determination of the binary isotope signature of B and Sr elements, it is possible to discriminate domestic rice from foreign-grown rice.
For domestic samples. Two sample groups of domestic brown-rice were from northeast Japan and southwest Japan near the boundary of Itoigawa-Shizuoka tectonic line. The binary isotope signatures of each sample were plotted (Fig. 4). The southwest Japan rice with the high Sr-IRs value (0.709) was distributed in the upper part of Fig. 4. Contrary to this, the northeast Japan rice with a range of ^{87}Sr/^{86}Sr ratios (0.706-0.707) tended to distribute in the lower part of Fig. 4. This may be
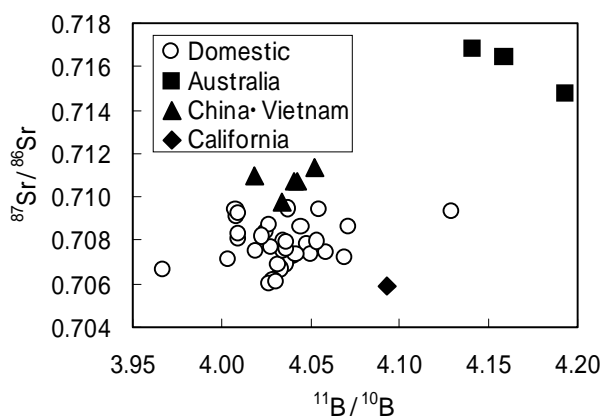

Fig. 3 Distributions of ^{11}B:^{10}B and ^{87}Sr: ^{86}Sr in whole brown-rice samples.

because Sr-IR of volcanic rocks in Japan is divided into northeast Japan and southwest Japan by the boundary of Itoigawa-Shizuoka tectonic line.[22] One sample with a high B-IR was harvested in Tanegashima-island, in the Kagoshima Prefecture. This rice crop was grown near the coast and it is possible that the B-IR of rice grown under the influence of seawater (^{11}B/^{10}B ratio in surface seawater: 4.217± 0.013[n=6] [23]) might be high.
Importance of Geographical Information regarding B-IR and Sr-IR. As described above, the possibility of discriminating domestic brown-rice from foreign-grown rice was indicated mainly by Sr-IRs, rather than by B-IRs. Geochronologically, parent material of the Japanese arc is younger than that of

Australia, China and Vietnam and is slightly older than that of California. Since older rocks have a higher ^{87}Sr/^{86}Sr ratio,[24] the high ^{87}Sr/^{86}Sr ratios in the samples yielded in Australia, China,
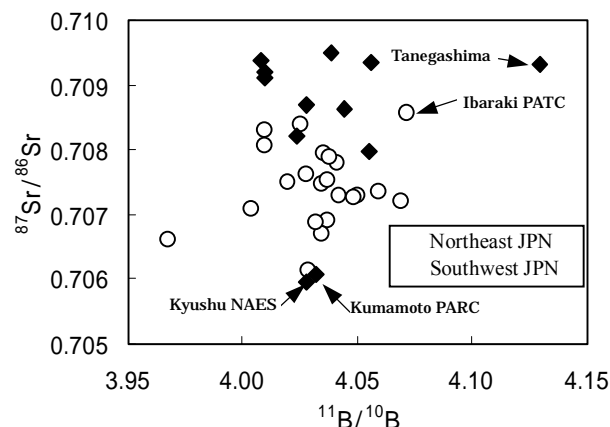

Fig. 4 Distribution of ^{11}B:^{10}B and ^{87}Sr:^{86}Sr in the domestic brown-rice samples. Tanegashima, Kagoshima Prefecture (Tanegashima) Ibaraki PATC, Ibaraki Prefecture Agricultural Training Center; Kyushu NAES, Kyushu National Agricultural Experiment Station; Kumamoto PARC, Kumamoto Prefecture Agricultural Research Center.

and Vietnam, and the low ^{87}Sr/^{86}Sr ratio in Californian sample are almost in line with expectations.

There is less geographical information regarding B-IR than Sr-IR, and the available information is limited to minerals[25-28] and to hot springs,[29] at least in Japan. This might be mainly due to the technical difficulties of B-IR determination i.e., by TIMS so far.
Evaluation of the Analytical Methods for B-IR and Sr-IR. The precision of value in the rice samples determined by the Sr-IR method (RSD(%)=0.056) was higher than those determined by the B-IR method (RSD(%)=0.203) for the dry ashing and 0.369 for the microwave-assisted digestion method. Therefore, the Sr-IRs measured by this method was sufficiently precise to detect the regional differences in the samples.

Regarding the time required to obtain the IR value in the rice samples, at 8 hours per day, it took about 8 days for the Sr-IR determination and about 2 days for the B-IR determination by the microwave-assisted digestion method (0.2 g sample). The disadvantage of extended time for the Sr-IR determination (6 days longer) was the result of sample preparation time for the heavy sample size (5 g). It is necessary to shorten the time for sample preparation procedures for the Sr-IR determination.

References

1. A. Yasui, K. Shindoh, *Bunseki Kagaku.,* **2000,** *49*, 405.

2. H. Takeda, H. Koga, S. Tamura, O. Katayama, *Sukairahkufuudosaiensu Kenkyusho Hohkoku*, **1996**, *No. 5*, 41.

3. A. Macos, A. Fisher, G. Rea, S. J. Hill, *J. Anal. At. Spectrom.*, **1998,** *13*, 521.

4. K. A. Anderson, B. A. Magnuson, M. L. Tschirgi, B. Smith, *J. Agric. Food Chem.*, **1999**, *47*, 1568.

5. M. J. Baxter, H. M. Crews, M. J. Dennis, I. Goodall, D. Anderson, *Food Chem.*, **1997**, *60*, 443.

6. A. Kawasaki and H. Oda, "*Plasma Source Mass Spectrometry, -New Developments and Applications*", ed. G. Holland and S. D. Tanner, **1999**, The Royal Society of Chemistry, Cambridge, UK, 173.

7. C. Tsutsumi, C. Shimomura, *Syokuhin-Sohgoh-Kenkyusho Kenkyusho Hohkoku*, **1978**, *No.33*, 12.

8. T. Ishikuro and N. Yamada, *Nihon-Dojohiryogaku-Zasshi*, **1997**, *68*, 629.

9. P. Horn, S. Hölzl, W. Todt and D. Matthies, *Isotopes Environ. Health Stud.*, **1998**, *34*, 31.

10. A. M. Almedia and M. T. Vasconcelos, *J. Anal. At. Spectrom.***, 2001**, *16*, 607.

11. E. Dambrine, M. Loubet, J.A. Vega and A. Lissarague, *Plant Soil*, **1997**, *192*, 129.

12. Y. Yokoo and T. Nakano, *Ann. Rep. Inst. Geosci.,Univ. Tsukuba*, **1996**, *22*, 37.

13. G. Åberg, *Water Air Soil Pollut.*, **1995**, *79*, 309.

14. D.C. Gregoire, *J. Anal. At. Spectrom.***, 1990**, *5*, 623.

15. A. Vengosh, K.G. Heumann, S. Juraske and R. Kasher, *Environ. Sci. Technol.*, **1994**, *28*, 1968.

16. I.T. Platzner, K. Habfast, A.J. Walder and A. Goetz, "*Modern isotope ratio mass spectrometry*", **1997**, John Wiley & Sons, Chichester, 289.

17. A. Kawasaki. and H. Oda, *Nihon-Dojyo-Hiryo-Gakkai Kohen Yohshishu*, **1999**, *45* 150, Sapporo, Japan.

18. A. Kawasaki, R. Kimura and S. Arai, *Commun. Soil Sci. Plant Anal*., **2000**, *31*, 2413.

19. A. Vengosh, A. R. Chivas, M. T. McCulloch, A. Starinsky and Y. Kolodny, *Geochim. Cosmochim. Acta,* **1991**, *55*, 2591.

20. Y. Asahara, T. Tanaka, H. Kamioka and A. Nishimura, *Earth Planet Sci. Lett.*, **1995**, *133*, 105.

21. G. Faure, "*Principles of isotope geology 2nd ed.* ", **1986**, John Wiley & Sons, New York, 161.

22. H. Kurasawa, *Chigaku Zasshi*, **1986**, *95*, 30.

23. R. L. Bassett, *Appl. Geochem.*, **1990**, *5*, 541.

24. R. C. Capo, B. W. Stewart and O. A. Chadwick, *Geoderma*, **1998**, *82*, 197.

25. M. Shima, *Geochim. Cosmochim. Acta,* **1963**, *27*, 911.

26. M. Shima, *Rikagaku-Kenkyusho Hohkoku*, **1963**, *39*, 207.

27. M. Nomura, T. Kanzaki, T. Ozawa, M. Okamoto and H. Kakihana, *Geochim. Cosmochim. Acta,* **1982**, *46*, 2403.

28. T. Kanzaki, M. Yoshida, M. Nomura, H. Kakihana and T. Ozawa, *Geochim. Cosmochim. Acta,* **1982**, *43*, 1859.

29. H. Kakihana, T. Ossaka, T. Oi, M. Musashi, M. Okamoto and M. Nomura, *Geochem. J*., **1987**, *21*, 133.