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NOTE

The $^3He/^4He$ ratio of the new internal He Standard of Japan (HESJ)

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We have prepared an artificial mixture of ^3He and ^4He to be used as an internal standard for precise $^3He/^4He$ measurements of terrestrial mantle-derived samples. The mixture is named HESJ (He Standard of Japan). The $^3He/^4He$ ratio of HESJ was determined by obtaining the weighted average of repeated analyses from five machines in four laboratories in Japan. The recommended value of the $^3He/^4He$ ratio of HESJ relative to the air value (R/Ra) is 20.63 ± 0.10. HESJ is available to all researchers.

INTRODUCTION

Precise analysis of $^3He/^4He$ ratios in terrestrial, mantle-derived samples has long been a primary focus of noble gas geochemistry (e.g., Ozima and Podosek, 1983). Such analyses have shown that Mid Oceanic Ridge Basalts (MORB) have uniform $^3He/^4He$ ratios that are higher than the air value (Ra) by about a factor of 8. In contrast, Oceanic Island Basalts (OIB) have variable and much higher value than the air value by a factor of about 12–30 (e.g., Farley and Neroda, 1998). Volcanic gases of mantle origin have ratios similar to those in MORB. Thus many terrestrial samples of mantle origin have $^3He/^4He$ ratios higher than the air value by about an order of magnitude.

The standard that is used for the analysis of helium isotopic ratios is very important for the accuracy and precision of these measurements. However, terrestrial air is commonly used as a helium standard, despite the fact that He is depleted in air, meaning that large amounts of air are needed to separate adequate amounts of He for analysis. In addition, the very low $^3He/^4He$ ratio in air (1.4×10^{-6}) means that a large amount of gas is needed in order to obtain sufficient ^3He to obtain a precise measurement of the $^3He/^4He$ ratio. Furthermore, the helium mass discrimination factor may be large if there is a substantial difference between the $^3He/^4He$ ratio in the unknown compared with the ratio in air. For this reason, some laboratories use natural volcanic gases

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with a ratio of ~10^{-5} as a standard for He isotopic measurement rather than air (e.g., Honda *et al.*, 1993).

A widely available internal standard that has a helium isotopic composition similar to the ratios in mantle-derived samples is clearly needed in the noble gas community. We have prepared an artificial mixture of ^{3}He and ^{4}He to be used as an internal standard for precise measurements of He isotopic ratios of terrestrial mantle-derived samples. We have named this new He standard HESJ (He Standard of Japan). This artificial mixture has the advantage of being sufficiently large that it can be used as an internal standard almost indefinitely by a number of different laboratories. In addition, because the standard is made of pure helium, it does not have to be purified prior to analysis. This short note provides the results of measurements of the ^{3}He/^{4}He ratio that were obtained in several different laboratories, and presents the recommend value of the ^{3}He/^{4}He ratio of HESJ.

Analytical Methods and Results

A pre-mixed volume of ^{3}He and ^{4}He was obtained from Nippon Sanso Co. through Osaka University. This mixture contained about 15 ppm ^{3}He in 99.9% pure ^{4}He. One litre of He was inlet into a 0.46 litre cylindrical tank with a 1/4 NPT screw at a temperature of 300 K. Thus the internal tank pressure of He was about 2.4 atm. Gas cylinders were distributed to four Japanese noble gas laboratories (Osaka University, Hiroshima University and two laboratories at The University of Tokyo). The condensed He in the cylinder was further prepared to the suitable specification in each laboratory. For example, at Osaka University, HESJ was inlet into a 1500 cm^3 tank with a pressure of about 10^{-3} Torr. We used a pippeted volume of 1.5 cm^3 from this tank for the He measurements. Thus, a 1 liter gas cylinder under 2.4 atm pressure is sufficient for tens of years worth of analyses.

The analytical methods performed by each laboratory have been reported previously (Wada and Matsuda, 1998; Aka *et al.*, 2001; Hanyu *et al.*, 1999; Sano *et al.*, 1998). Measurements of HESJ at the different laboratories were carried out using VG5400 noble gas mass spectrometers, except at Hiroshima University where a Nuclide Co. (6-60-SGA) mass spectrometer was used. The measurements at Osaka University and the Earthquake Research Institute at The University of Tokyo were carried out on commercial VG5400s. In contrast, a modified VG5400 machine (MS-III) and a similar instrument with split tube double collectors (MS-IV) were used at the Laboratory for Earthquake Chemistry at The University of Tokyo. The precise description of the modifications to the MS-IV and of the measurements using the MS-IV were given by Sumino *et al.* (2001).

In all measurements except those from the MS-III at the Laboratory for Earthquake Chemistry, air was used as a primary standard for the determination of the ^{3}He/^{4}He ratio of HESJ. The errors in the obtained He isotopic ratios of HESJ are mainly from that in the measurement of primary standard of air because of the low ^{3}He content in air. At Osaka University, each of the seven measurements of HESJ was corrected for mass discrimination using an air standard analysis determined prior to each measurement of HESJ. From the Laboratory for Earthquake Chemistry, fifteen measurements were carried out using the MS-IV machine at two different time periods, and the calculated average ^{3}He/^{4}He ratio is from fourteen measurements, excluding the lowest value measured at the highest pressures (Sumino *et al.*, 2001). At the Earthquake Research Institute, ten analyses of HESJ were corrected using six measurements of the primary air standard. At Hiroshima University, twelve measurements of HESJ were corrected using five measurements of the air standard. The data value from Hiroshima has the lowest ratio with largest error. This may be because the measurement was performed on a 6-inch radius mass spectrometer (6-60-SGA) which is not good enough to completely separate ^{3}He and HD with flat peak shapes (Sano *et al.*, 1982).

In contrast, an air standard was not used to correct the two measurements of HESJ performed on the MS-III at the Laboratory for Earthquake

Table 1. The $^3He/^4He$ ratio of HESJ (He Standard of Japan)

Laboratory		Number of measurements	$^3He/^4He$ (R/Ra)
Osaka University[1)]		7	20.46 ± 0.35
Laboratory for Earthquake Chemistry (The University of Tokyo)	MS-III[2)]	2	20.66 ± 0.11 20.61 ± 0.16
	MS-IV[3)]	14	20.77 ± 0.24
Earthquake Research Institute[1)] (The University of Tokyo)		10	20.66 ± 0.69
Hiroshima University[4)]		12	20.39 ± 0.89
Recommended value[5)]			20.63 ± 0.10

[1)]Commercial VG5400.
[2)]Modified VG5400 using an artificial standard with a $^3He/^4He$ ratio of 1.71×10^{-4}.
[3)]Modified VG5400 with split tube double collectors (Sumino et al., 2001).
[4)]Mass spectrometer (6-60-SGA) of Nuclide Co.
[5)]Weighted mean of above six data values.

Chemistry. Instead, these measurements were corrected using an artificial standard with a $^3He/^4He$ ratio of 1.71×10^{-4}. Because this artificial mixture has a high concentration of ^3He, the assigned errors for these measurements are small compared to those of other results.

The $^3He/^4He$ ratios of HESJ from each of the four laboratories are listed in Table 1 and Fig. 1. As the measurements are different in each laboratory we list only the final results (see Appendix for the individual measurement results in each laboratory). The assigned errors are one sigma for repeated analyses except for the two measurements obtained by MS-III at the Laboratory for Earthquake Chemistry because it is not possible to obtain statistically meaningful uncertainties from two measurements. These two measurements from the MS-III have small errors and are listed individually.

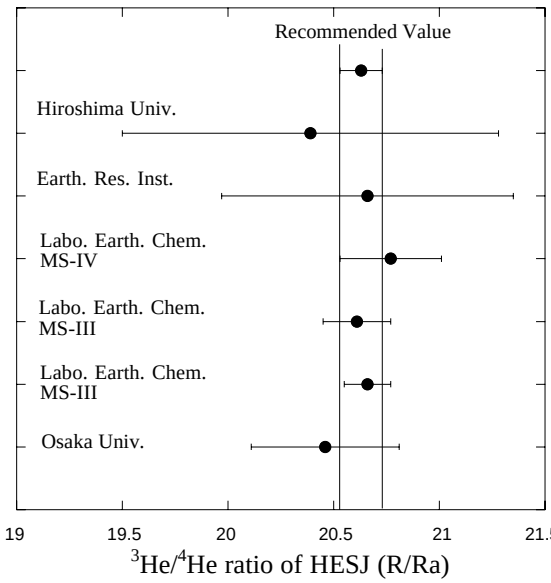

Fig. 1. Comparison of $^3He/^4He$ ratios of HESJ (He Standard of Japan) as measured by five mass spectrometers in four laboratories and the recommended value for the internal standard.

THE RECOMMENDED $^3He/^4He$ FOR HESJ

The six $^3He/^4He$ ratios of HESJ obtained from five different mass spectrometers in four laboratories agree within one sigma uncertainty. We thus calculated the weighted means from the reciprocal of the standard deviation from these six values. The recommended value of $^3He/^4He$ ratio of HESJ relative to the air value (R/Ra) is 20.63 ± 0.10. When we calculate the mean value without

the Hiroshima value (which has large uncertainties), the obtained mean value is 20.64 ± 0.09, indicating that the large uncertainty from the analyses obtained at Hiroshima University does not significantly affect the calculated weighted mean of the reciprocal of the standard deviation.

To ensure that the use of different standards (air versus an artificial helium mixture in the measurements by MS-III at the Laboratory for Earthquake Chemistry) does not influence the measured ratio of HESJ owing to uncertainties in the mixing ratio of the artificial standard, we calculated the mean $^3He/^4He$ ratio of HESJ using only the three measurements obtained from laboratories that used the air standard. The mean value from these analyses is 20.65 ± 0.20, which is within uncertainty of the value of 20.63 ± 0.10 calculated from all six measurements, as well as of the values of the two individual measurements using MS-III of 20.66 ± 0.11 and 20.61 ± 0.16.

Thus we conclude that 20.63 ± 0.10 is the best estimate for the $^3He/^4He$ ratio of HESJ. The assigned error is relatively small enough compared with the standard deviation in individual measurements with a reasonable output signal of He. The $^3He/^4He$ ratio of HESJ is now sufficiently well-determined to be used as an internal standard for measurement of He isotopic ratios among different laboratories. HESJ has already been used as an internal standard in a few investigations (Matsumoto *et al*., 2001; Maruoka *et al*., 2001).

HESJ is available for distribution to laboratories in need of a standard for precise He measurement. HESJ has already been distributed to the three laboratories in Australia, China and Taiwan. Please contact one of these authors for details on how to prepare the necessary tank and valves.

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REFERENCES

Aka, F. T., Kusakabe, M., Nagao, K. and Tanyileke, G. (2001) Noble gas isotopic compositions and water chemistry of soda springs from the islands of Bioko, Sao Tome and Annobon, along with Cameroon Volcanic Line, West Africa. *Appl. Geochem.* **16**, 323–338.

Farley, K. A. and Neroda, E. (1998) Noble gases in the Earth's mantle. *Ann. Rev. Earth Planet. Sci*. **26**, 189–218.

Hanyu, T., Kaneoka, I. and Nagao, K. (1999) Noble gas study of HIMU and EM ocean island basalts in the Polynesian region. *Geochim. Cosmochim. Acta* **63**, 1181–1201.

Honda, M., McDougall, I., Patterson, D. B., Doulgeris, A. and Clague, D. A. (1993) Noble gases in submarine pillow basalt glasses from Loihi and Kilauea, Hawaii: a solar component in the Earth. *Geochim. Cosmochim. Acta* **57**, 859–874.

Maruoka, T., Matsuda, J. and Kurat, G. (2001) Abundance and isotopic composition of noble gases in metal and graphite of the Bohumilitz IAB iron meteorite. *Meteorit. Planet. Sci.* **36**, 597–609.

Matsumoto, T., Chen, Y. and Matsuda, J. (2001) Concomitant occurrence of primordial and recycled noble gases in the Earth's mantle. *Earth Planet. Sci. Lett*. **185**, 35–47.

Ozima, M. and Podosek, F. A. (1983) *Noble Gas Geochemistry*. Cambridge Univ. Press, 367 pp.

Sano, Y., Tominaga, T., Nakamura, Y. and Wakita, H. (1982) $^3He/^4He$ ratios of methane-rich natural gases in Japan. *Geochem. J*. **16**, 237–245.

Sano, Y., Nishio, Y., Sasaki, S., Gamo, T. and Nagao, K. (1998) Helium and carbon isotope systematics at Ontake volcano, Japan. *J. Geophys. Res*. **103**, 23863–23873.

Sumino, H., Nagao, K. and Notsu, K. (2001) Highly sensitive and precise measurement of helium isotopes using a mass spectrometer with double collector system. *J. Mass Spectrom. Soc. Jpn*. **49**, 61–68.

Wada, N. and Matsuda, J. (1998) A noble gas study of cubic diamonds from Zaire: constraints on their mantle source. *Geochim. Cosmochim. Acta* **62**, 2335–2345.

APPENDIX

(1) Measurements from Osaka University.

Sample	^{4}He Output voltage (V)	^{3}He/^{4}He (R/Ra)
HESJ	0.5725	19.89 ± 0.19
	0.5627	20.67 ± 0.20
	0.5802	20.17 ± 0.23
	0.5467	20.49 ± 0.32
	0.2943	20.33 ± 0.30
	0.9604	20.77 ± 0.29
	0.4680	20.87 ± 0.30
	Average	20.46 ± 0.35

(2) Measurements from the Laboratory for Earthquake Chemistry (modified from table 3 in Sumino *et al*., 2001).

(a) Using MS-III.

Sample	^{4}He Output voltage (V)	^{3}He/^{4}He (R/Ra)
HESJ	0.0645	20.66 ± 0.11
	0.0675	20.61 ± 0.16

(b) Using MS-IV.

Sample	^{4}He Output voltage (V)	^{3}He/^{4}He (R/Ra)
HESJ	0.03055	21.15 ± 0.41
	1.145	20.23 ± 0.23*
	0.03000	20.94 ± 0.36
	0.5490	20.36 ± 0.23
	0.2617	20.52 ± 0.24
	0.1242	20.77 ± 0.26
	0.01465	21.16 ± 0.49
	0.02935	21.01 ± 0.36
	0.03802	20.45 ± 0.33
	0.01959	20.68 ± 0.36
	0.02463	20.87 ± 0.45
	0.07783	20.64 ± 0.32
	0.09519	20.73 ± 0.30
	0.5549	20.69 ± 0.26
	0.1469	20.78 ± 0.29
	Average	20.77 ± 0.24

(Excluding the second measurement marked with *.)

(3) Measurements from the Earthquake Research Institute.

Sample	^{4}He Output voltage (V)	^{3}He/^{4}He
HESJ	0.2956	0.2220 ± 0.0018
	0.1209	0.2189 ± 0.0060
	0.05237	0.2264 ± 0.0034
	0.1166	0.2225 ± 0.0033
	0.1561	0.2229 ± 0.0032
	0.05511	0.2221 ± 0.0035
	0.1608	0.2232 ± 0.0029
	0.05814	0.2198 ± 0.0022
	0.08608	0.2197 ± 0.0033
	0.03357	0.2244 ± 0.0046
	Average	0.2222 ± 0.0023

The average value of six measurements for air was 0.01075 ± 0.00034 at the ^{4}He output voltage of around 0.2 V.
Thus, (R/Ra) of HESJ = 20.66 ± 0.69.

(4) Measurements from Hiroshima University.

Sample	^{4}He Output voltage (V)	^{3}He/^{4}He ($\times 10^{-6}$)
HESJ	0.66	28.83 ± 0.58
	0.43	28.76 ± 0.60
	0.72	29.07 ± 0.32
	0.65	30.63 ± 1.16
	0.56	29.79 ± 0.92
	0.47	29.20 ± 1.26
	0.43	30.62 ± 0.70
	0.05	30.00 ± 1.29
	0.31	29.87 ± 0.96
	0.06	28.06 ± 2.58
	0.19	30.64 ± 0.70
	0.19	30.51 ± 1.01
	Average	29.67 ± 0.87

The average value of five measurements for air was 1.455 ± 0.047 ($\times 10^{-6}$).
Thus, (R/Ra) of HESJ = 20.39 ± 0.89.