

## COMMENT ON "A TEN-YEAR DECREASE IN THE ATMOSPHERIC HELIUM ISOTOPE RATIO POSSIBLY CAUSED BY HUMAN ACTIVITY", by Y. Sano et al.

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In a recent paper, *Sano et al.* [1989] reported a 1-2% decrease in the atmospheric  $^3\text{He}/^4\text{He}$  ratio over a 10-year period. They based this conclusion on helium isotope measurements of 17 air samples collected at various sites in Japan during the period from 1977 to 1988. Furthermore, in an earlier paper *Sano et al.* [1988] reported an absolute determination of the atmospheric  $^3\text{He}/^4\text{He} = (1.343 \pm 0.013) \times 10^{-6}$  for air collected at Ueno Park, Central Tokyo, Japan, in August, 1988. This represents an even larger decrease (~3.4%) in  $^3\text{He}/^4\text{He}$  relative to the accepted value of  $1.39 \times 10^{-6}$ , which is the average of two previous measurements of the atmospheric helium isotope ratio by *Mamyrin et al.* [1970] and by *Clarke et al.* [1976]. A decrease in the atmospheric helium isotope ratio over time has serious implications for the field of helium isotope geochemistry, since virtually every laboratory engaged in helium isotope measurements uses samples of air helium as a natural isotopic standard. The use of air helium as a standard is based on the assumption that the atmospheric helium isotope ratio is invariant with respect to time and geographical location, due to the long residence time of helium in the atmosphere (~ $10^6$  years) relative to the atmospheric mixing time (~10 years). Furthermore, the 1-4% decrease reported by *Sano et al.* [1988, 1989] is a large effect considering that modern mass spectrometers are capable of measuring deviations in terrestrial  $^3\text{He}/^4\text{He}$  ratios as small as 0.2% [*Lott and Jenkins*, 1984; *Lupton*, 1990]. While *Sano et al.* [1988, 1989] admit that the observed  $^3\text{He}/^4\text{He}$  decrease may be due to experimental artifacts or to local contamination of Tokyo air with industrial gases enriched in radiogenic helium, they discuss several other explanations, including a global decrease in atmospheric  $^3\text{He}/^4\text{He}$  due to anthropogenic release of crustal helium. In this note we examine the evidence for changes in the atmospheric  $^3\text{He}/^4\text{He}$  ratio, and conclude that the existing data, when evaluated in concert with their associated errors, are consistent with a zero rate of change in atmospheric  $^3\text{He}/^4\text{He}$ .

First, we find no evidence in any of the data presented by *Sano et al.* [1988, 1989] that the atmospheric helium isotope ratio is changing with time. An absolute determination of the  $^3\text{He}/^4\text{He}$  ratio in air requires the fabrication of a synthetic helium isotope standard of known isotopic composition.

This is an exceedingly difficult task due to the low abundance of  $^3\text{He}$  relative to  $^4\text{He}$ , and thus it is not surprising that the absolute determination of air  $^3\text{He}/^4\text{He}$  by *Sano et al.* [1988] does not agree with the measurements of *Mamyrin et al.* [1970] and *Clarke et al.* [1976]. On the other hand, the more recent measurements by *Sano et al.* [1989] of the air helium isotopic composition relative to a running standard are much more compelling, since these results do not depend on the absolute accuracy of a synthetic standard. Figure 1a shows the data from *Sano et al.* [1989] plotted with  $2\sigma$  error bars in order to provide a 95% confidence interval for their data points. The figure illustrates the fact that the  $\pm 1.96\%$  ( $2\sigma$ ) average precision which they report for each determination is greater than the total decrease in  $^3\text{He}/^4\text{He}$  of ~0.9% they claim to see over the ten-year period. *Sano et al.* [1989] fitted a least-squares straight line to their data after excluding one analysis of California air from the data set. This fit was done properly by including consideration of the errors associated with each data point. The result was an estimated rate of decrease of  $^3\text{He}/^4\text{He}$  of  $(0.080 \pm 0.115) \%$ /year ( $2\sigma$  error), which is not statistically different from a zero time rate of change.

In addition to the measurements of *Sano et al.*, there are two other pieces of evidence indicating little or no change in the atmospheric  $^3\text{He}/^4\text{He}$  ratio during the last two decades. The first consists of a recent determination of the absolute  $^3\text{He}$  content of air by *Davidson and Emerson* [1990]. When combined with an earlier measurement of the atmospheric  $^4\text{He}$  abundance [*Holland and Emerson*, 1987], this provides an additional recent determination of the atmospheric  $^3\text{He}/^4\text{He}$  ratio of  $(1.393 \pm 0.014) \times 10^{-6}$  ( $2\sigma$ ). We estimated the uncertainty in this result by first computing the standard deviation of the mean ( $n=7$ ) of the determinations of atmospheric  $^3\text{He}$  concentration reported by *Davidson and Emerson* [1990], and then properly combining this uncertainty with that reported for the air  $^4\text{He}$  concentration reported by *Holland and Emerson* [1987]. Table 1 summarizes the three absolute determinations of the atmospheric  $^3\text{He}/^4\text{He}$  ratio spanning 19 years from 1969 to 1988. A linear regression fit to these data, including consideration of the errors associated with each determination, yields a slope of  $(-0.0067 \pm 0.14) \%$ /yr ( $2\sigma$ ) for the rate of change in the  $^3\text{He}/^4\text{He}$  ratio. Although the error associated with this slope is too large to provide a critical constraint on the results of *Sano et al.* [1989] discussed here, we decided to include discussion of these absolute determinations because they are additional data consistent with zero rate of change.

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The second additional constraint on the rate of change of atmospheric  $^3\text{He}/^4\text{He}$  is based on repeated comparisons of California marine air against a secondary helium isotope standard, namely the "Murdering Mudpots" (MM) geothermal gas sample collected from the Mud Volcano area of Yellowstone Park [Welhan, 1981; Welhan et al., 1988]. These measurements, which are plotted in Figure 1b and summarized in Table 2, were carried out during the routine calibration of air standards on helium isotope mass spectrometers at the Scripps Institution of Oceanography (SIO) and here at U.C. Santa Barbara (UCSB). Both mass spectrometer systems employ a low temperature ( $\sim 40^\circ\text{K}$ ) charcoal trap to separate He from Ne, and each system has both an air standard and the MM geothermal standard housed in stainless steel aliquoting systems for calibrating the  $^3\text{He}/^4\text{He}$  response of the mass spectrometer.

The earliest sample of California marine air reported here was collected in 1973, when one of us (JL) filled an evacuated stainless steel tank with air at the end of the SIO pier, and that air sample has been used as an isotopic standard on the SIO helium mass spectrometer since that date. Of more relevance to the present discussion, the helium isotopic ratio of the MM geothermal standard has been repeatedly compared against this 1973 SIO air standard, and found to be  $R_{\text{MM}}/R_{\text{air}} = 16.45 \pm 0.12$  ( $2\sigma$ ), where  $R = ^3\text{He}/^4\text{He}$  [Rison and Craig, 1983; Poreda et al., 1988; Poreda and Craig, 1989; Poreda, private comm.]. (In order to indicate changes in the atmospheric helium isotope ratio,

we have plotted the inverse ratio  $R_{\text{air}}/R_{\text{MM}}$  in Figure 1b). We have plotted this SIO data point at 1973 in Figure 1b, since we believe it is a valid measure of the helium isotopic composition of California air collected in that year. In 1980 another sample of SIO pier air was collected and measured against the 1973 air standard, and the  $^3\text{He}/^4\text{He}$  ratios were found to agree to  $\pm 0.5\%$ , indicating that the process of taking aliquots from the 1973 air standard had not compromised its integrity.

In addition to this 1973 determination, we have made four additional helium isotope measurements of California air in 1985, 1987, 1988, and 1990 in the course of calibrating the size of the air aliquot on the UCSB mass spectrometer system (Table 2). During each calibration a sample of marine air was collected from the end of the Goleta pier in an evacuated stainless steel cylinder, and then compared against the MM geothermal standard and the air aliquot running standard on the UCSB mass spectrometer. Each of the values reported in Table 2 and shown in Figure 1b is the result of a dozen or so direct mass spectrometer comparisons between an air sample and the MM geothermal standard. The errors associated with each determination of  $R_{\text{air}}/R_{\text{MM}}$  include statistical variations in the measurement of air samples and of aliquots of the MM geothermal standard. However, because these are direct comparisons between air samples and a secondary standard, and since we are reporting the results as the ratio  $R_{\text{air}}/R_{\text{MM}}$ , the uncertainty in the absolute value of  $R_{\text{MM}}$  does not enter into the error

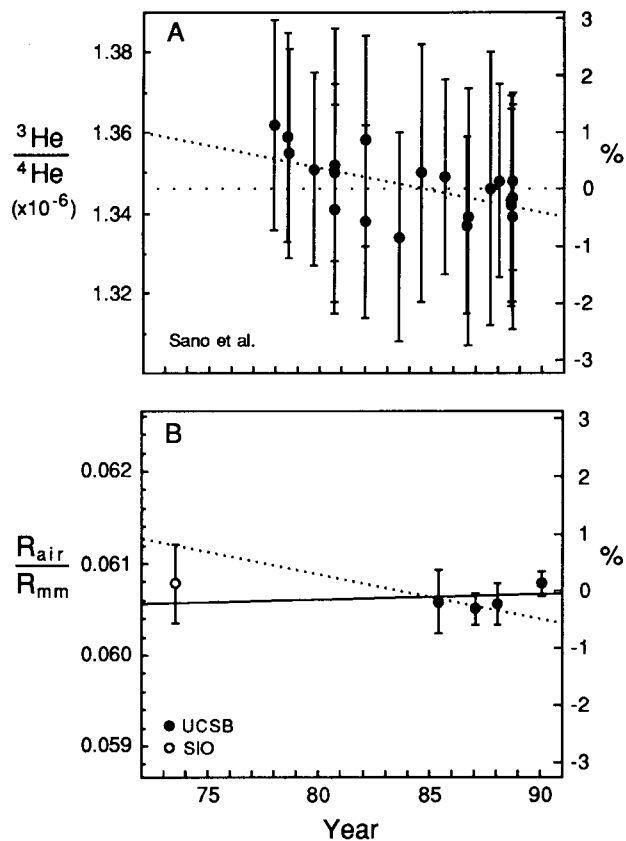


Figure 1. a) Absolute  $^3\text{He}/^4\text{He}$  of air samples vs. time of collection. Data taken directly from Sano et al. [1989], except plotted with  $2\sigma$  error bars. Note that we have used the data as presented in Fig. 2 of Sano et al. [1989], rather than from their Table 1, which apparently contains a typographical error for sample No. 20. The right hand axis shows the percentage deviation of the ratio from the mean value of  $^3\text{He}/^4\text{He} = 1.347 \times 10^{-6}$ , which is also indicated by the dotted horizontal line. The heavier dotted line is a least-squares fit to their data, which yields a slope of  $-0.080 \pm 0.115$  %/year ( $2\sigma$ ). This indicates that their data, because of the relatively large errors, are consistent with a zero time rate of change of  $^3\text{He}/^4\text{He}$  at the 95% confidence level.

b) Helium isotope ratio in samples of California marine air, measured relative to the MM geothermal gas standard plotted vs. date of collection of the air samples. Measurements were made on similar systems at SIO (open circle) and at UCSB (closed circles). Data are listed in Table 2 and are plotted as  $R_{\text{air}}/R_{\text{MM}}$ , where  $R = ^3\text{He}/^4\text{He}$ . All error bars are  $2\alpha$ . The right hand axis indicates percentage deviation from the mean value of  $R_{\text{air}}/R_{\text{MM}} = 0.060652$ . The solid line is a least-squares fit to the SIO plus UCSB data, which yields a slope of  $0.0093 \pm 0.043$  %/year ( $2\sigma$ ). The regression line of Sano et al. [1989] (dotted line) is shown for comparison. Note that the vertical scales in Figures 1a and 1b have been adjusted to show identical percentage deviations in  $^3\text{He}/^4\text{He}$ .

Table 1. Absolute determinations of the  $^3\text{He}/^4\text{He}$  ratio in air.

Group	Year	$^3\text{He}/^4\text{He}$ ( $\times 10^6$ )	$2\sigma$
<i>Mamyrin et al.</i>	1969	1.399	.026
<i>Clarke et al.</i>	1975	1.384	.012
<i>Davidson et al.</i>	1988	1.393	.028

Table 2. Marine air relative to the MM He isotope standard.

Date	$R_{\text{air}}/R_{\text{MM}}$	$2\sigma$	$\Delta$ (%) <sup>a</sup>
1973 <sup>b</sup>	0.06079	0.00042	+0.228
22 May 1985	0.06059	0.00035	-0.100
11 Feb 1987	0.06051	0.00017	-0.221
12 Feb 1988	0.06057	0.00022	-0.130
18 Jan 1990	0.06078	0.00014	+0.223

<sup>a</sup>  $\Delta = \{[(R_{\text{air}}/R_{\text{MM}})/r] - 1\} \times 100$ , where  $r = 0.060652$  ( $n=5$ ), the mean of the  $R_{\text{air}}/R_{\text{MM}}$  values.

<sup>b</sup> measured at SIO. From *Rison and Craig* [1983], *Poreda et al.* [1988], *Poreda and Craig* [1989], and Poreda [private comm.].

calculations. It is important to note that the MM geothermal gas standards used on the SIO and UCSB mass spectrometers are both splits of Yellowstone Park sample YP-123 collected in June of 1979 [Welhan, 1981], and thus helium isotope determinations made on the SIO and UCSB instruments should be directly comparable as long as they are reported relative to the MM geothermal standard. It should also be noted that the three mass spectrometer systems discussed here have quite different precision for a single helium isotope determination: ~2% for Univ. of Tokyo, ~1% for SIO, and ~0.4% for the UCSB instrument (all  $2\sigma$  errors).

As summarized in Figure 1b, the helium isotope ratios of California marine air measured relative to the MM geothermal standard exhibit very little change over the period from 1973 to 1990. A least-squares straight line fitted to the data in Table 2 (see Figure 1b), including consideration of the errors associated with each determination, gives a slope of  $(0.0093 \pm 0.043) \%$ /year ( $2\sigma$ ). Although this slope is positive, suggesting an increase in the  $^3\text{He}/^4\text{He}$  ratio, this result is also consistent with zero time rate of change in the atmospheric  $^3\text{He}/^4\text{He}$  ratio. At the 95% confidence interval we can say that the rate of change of air  $^3\text{He}/^4\text{He}$  is between -0.034%/year and +0.052%/year.

In conclusion, having considered 1) the data of *Sano et al.* [1988, 1989], 2) the absolute determinations of  $^3\text{He}/^4\text{He}$  by

*Mamyrin et al.* [1970], *Clarke et al.* [1976], and *Davidson and Emerson* [1990], and 3) the comparisons made at SIO and UCSB between California marine air against an independent standard, we find no evidence that the atmospheric helium isotope ratio is changing with time. It is possible that air in Japan has been affected by addition of radiogenic helium while California air has not, but this seems unlikely, since the two measurements of California air reported by *Sano et al.* [1989] fit into the pattern of their measurements of Japan air. The strongest constraints on the rate of change come from the SIO and UCSB measurements of California air, which show that the rate of change is less than  $\pm 0.05\%$ /year, with a best estimate very close to zero rate of change. Thus the time rate of change of air  $^3\text{He}/^4\text{He}$  is more than a factor of four lower than the rate of decrease reported in *Sano et al.* [1988] in their earlier paper, and at least a factor of 2 lower than the 0.08%/year reported by *Sano et al.* [1989]. Although no changes in atmospheric  $^3\text{He}/^4\text{He}$  have been observed which are outside the analytical precision, the high accuracy attainable with modern helium isotope mass spectrometers suggests that, if high integrity samples of old air can be obtained, it may be possible to resolve temporal changes in the atmospheric  $^3\text{He}/^4\text{He}$  ratio, or to place greater constraints on possible changes in this ratio over time.

*Notes Added In Proof.* After this Comment was accepted for publication, we performed the following additional analyses which bear on this subject:

1. In January of 1991 we performed an additional intercalibration of California marine air (from the Goleta pier) vs. the MM geothermal standard on the UCSB mass spectrometer. The result was  $R_{\text{air}}/R_{\text{MM}} = 0.06055 \pm 0.00011$  ( $2\sigma$ ), in agreement with the other determinations. If this value is added to the others listed in Table 2, a linear regression fit including consideration of the errors gives a time rate of change of  $-0.0074 \pm 0.0372 \%$ /yr ( $2\sigma$ ), which is not statistically different from the previous fit and is consistent with zero time rate of change.

2. We have analyzed the statistical variation for repeated measurements of the Univ. of Tokyo running standard as shown in Figure 1 of *Sano et al.* [1989]. This analysis indicates that they may have slightly overestimated the standard deviation associated with a single  $^3\text{He}/^4\text{He}$  measurement on their mass spectrometer, which they reported to be  $1\sigma = 1\%$  in their original paper. Accepting the idea that the linear regression line (Fig. 1 of *Sano et al.* [1989]) represents the average drift in their mass spectrometer, we measured the deviation of these  $R_s$  values from the regression line. Analysis of these deviations yields  $1\sigma = 6.39 \times 10^{-5}$ , and dividing this by their mean  $R_s$  of  $96.5 \times 10^{-4}$  gives  $1\sigma = 0.66\%$  for the estimated error for a single analysis on the Tokyo instrument. This error applies to both analyses of standards and samples, and thus the error for  $R/R_s$ , when combined in quadrature, gives  $2\sigma = 1.87\%$  at the 95% confidence interval, which is slightly lower than the 1.96% we have used for the calculations in this paper.

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