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# Time rate of atmospheric $^3\text{He}/^4\text{He}$ change: Constraint from South Pacific deep seawater

By

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with 3 Tables and 2 Figures

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(received, March 6, 1998)

**Abstract:** A recent study of atmospheric  $^3\text{He}/^4\text{He}$  ratio has suggested that it is decreasing with time, perhaps due to anthropogenic release from oil and natural gas wells of crustal helium with a low  $^3\text{He}/^4\text{He}$  ratio. A couple of objections have been made against this hypothesis based on new observations. It is important to verify the time rate of atmospheric  $^3\text{He}/^4\text{He}$  change, since this has serious implications for the field of helium isotope geochemistry. I present here the time rate change of  $-0.094 \pm 0.156$  %/year ( $2\sigma$  errors) based on the  $^3\text{He}/^4\text{He}$  ratio obtained from South Pacific deep seawater. Taking into account four other independent measurements on the time rate, I can calculate the average time rate of  $-0.028 \pm 0.030$  %/year ( $2\sigma$ ), which is consistent with a zero rate of change in atmospheric  $^3\text{He}/^4\text{He}$  ratio. However the average time rate is also consistent with the time rate of  $-0.033$  %/year estimated from anthropogenic release of crustal helium. Thus the problem is not yet solved and further study is desirable.

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## I. Introduction

The terrestrial atmosphere contains helium with a concentration of 5.24 ppm by volume (Ozima and Podosek, 1983). This is attributed to the balance between the supply from the solid Earth and escape from the top of the atmosphere into space (Kockarts, 1973). Since the residence time of helium in the atmosphere is approximately  $10^6$  years and is significantly longer than the mixing time in the atmosphere (~10 years), the air  $^3\text{He}/^4\text{He}$  ratio is believed to be a constant on a global scale (Lupton, 1983). However, recent human activity in fossil fuel extraction could release appreciable amount of crustal helium with a low  $^3\text{He}/^4\text{He}$  ratio (Oliver et al., 1984). Thus, the atmospheric  $^3\text{He}/^4\text{He}$  ratio could be decreasing with time, due to the anthropogenic release of crustal helium. If this is the case, it has serious implications for helium isotope geochemistry, since most laboratories engaged in helium isotope measurements use atmospheric helium as a natural isotopic standard (Lupton, 1983; Lupton and Graham, 1991).

Several recent papers, Sano et al. (1988), Sano et al. (1989), Lupton and Graham (1991), Sano et al. (1991), Hoffman and Nier (1993) have addressed the question of whether the atmospheric  $^3\text{He}/^4\text{He}$  ratio is decreasing with time. In the most recent paper, Hoffman and Nier (1993) reported no decrease in the atmospheric  $^3\text{He}/^4\text{He}$  ratio over a 32 year period. However controversy surrounds the subject. Sano et al. (1995) have measured  $^3\text{He}/^4\text{He}$  ratios of South Pacific deep seawater, where data were expressed relative to atmospheric helium collected in Chiba, Japan in August 1992. I compare the data with  $^3\text{He}/^4\text{He}$  ratios of Pacific deep seawater relative to the California marine air helium in 1973 (Lupton and Graham, 1991), which may provide constraint on the time rate of atmospheric  $^3\text{He}/^4\text{He}$  change.

## II. Precision of $^3\text{He}/^4\text{He}$ measurements

Helium was not separated from neon in Sano et al. (1995), which may introduce a small error in the apparent  $^3\text{He}/^4\text{He}$  ratio in the seawater samples (Rison and Craig, 1983). Sano and Wakita (1988) reported a negative correlation between the  $^3\text{He}/^4\text{He}$  and  $^{20}\text{Ne}/^4\text{He}$  ratios in the air standard. Since the  $^{20}\text{Ne}/^4\text{He}$  ratio of seawater is similar to that of air, the possible interference from neon to helium isotope measurement may be small. In order to check the interference, Sano et al. (1995) have measured air saturated distilled water at 20 °C and surface sea water samples collected in the South Pacific Ocean.

Helium contents and  $^3\text{He}/^4\text{He}$  ratios of three distilled water and two surface seawater samples reported by Sano et al. (1995) are listed in Table 1 together with some reference data (Benson and Krause, 1980; Ozima and Podosek, 1983; Ostlund et al., 1987). Discrepancy of the  $^3\text{He}/^4\text{He}$  ratio from the reference is less than 0.35% for distilled water and

Table 1. Helium contents and isotopic compositions of air saturated distilled water and surface seawater.

Sample	$^4\text{He}$ ( $\times 10^{-8}$ cm <sup>3</sup> STP/g)	$^3\text{He}/^4\text{He}$ ( $R_{\text{atm}}$ )
Air saturated water at 20°C		
No. 1	4.72	0.9743
No. 2	4.85	0.9924
No. 3	4.94	0.9865
Average	4.84	0.9844
Reference	4.5 <sup>a</sup>	0.9837 <sup>b</sup>
Surface seawater		
SA-6	3.92	0.9875
SA-7	3.68	0.9959
Average	3.80	0.9917
Reference	3.84 <sup>a</sup>	0.9885 <sup>c</sup>

a: from Ozima and Podosek (1983)

b: from Benson and Krause (1980)

c: from Ostlund et al. (1987)

seawater samples, when I take into account the average value. The precision for the  $^3\text{He}/^4\text{He}$  measurements, based on the reproducibility of air standard is about 0.7% (1  $\sigma$ ) during that time. Thus the discrepancy is smaller than the precision of measurements and ambiguity aroused from interference of neon to helium isotope measurement is negligibly small, even though Sano et al. (1995) did not separate helium from neon. This is partly due to the tuning of mass spectrometer (Lupton and Craig, 1987) and is also due to similarity of helium/neon ratios between air and seawater samples (Sano and Wakita, 1988), which may compensate the interference. Lupton and Craig (1987) suggested that the helium-neon interference is less than 1 % based on 90 selected seawater sample measurements, which is consistent with this work. Since the determination of  $^3\text{He}/^4\text{He}$  ratio for seawater sample includes measurement errors for both the sample itself and for the air standard, I take a total precision of 1% (1  $\sigma$ ) for the  $^3\text{He}/^4\text{He}$  ratio reported in Sano et al. (1995).

## III. $^3\text{He}/^4\text{He}$ ratios of Pacific deep seawater

It is well documented that South Pacific deep seawater has an extensive plume of water with excess  $^3\text{He}$  due to an injection of mantle derived helium at the spreading center axis on the East Pacific Rise (Lupton and Craig, 1981; Ostlund et al., 1987). The  $^3\text{He}$  plume can be traced over 2000 km to the west (Lupton and Craig, 1981). GEOSECS Pacific Expedition data revealed that the  $^3\text{He}$  plume is observed at the site 5000 km to the west where maximum excess  $^3\text{He}$  of approximately 25 % is found at a depth of about 2300 m

(Ostlund et al., 1987). Sano et al. (1995) have measured the  $^3\text{He}/^4\text{He}$  ratios of 10 seawater samples with varying depth collected at the site SA-6 ( $6^{\circ}36'S$ ,  $153^{\circ}36'E$ ) and 9 samples at SA-7 ( $14^{\circ}15'S$ ,  $154^{\circ}20'E$ ) on the KH-92-4 cruise of the Research Vessel, Hakuho Maru of the University of Tokyo. Figure 1 shows excess  $^3\text{He}$  profiles at the site SA-6 and SA-7 in South Pacific. Profiles of GEOSECS sites 251 and 263 are also shown for the comparison. There is an apparent excess  $^3\text{He}$  of about 25 % at the depth of 2200 m at sites SA-6 and SA-7, which is similar to those observed in GEOSECS Pacific Expedition. This suggests that the  $^3\text{He}$  plume may be traced over very long distance of about 9000 km to the west from the East Pacific Rise (Sano et al., 1995).

similar latitude, respectively. The observed excess  $^3\text{He}$  is mostly 1.5% - 2.0% larger at sites SA-6 and SA-7 than those of GEOSECS data (Figure 1). This is contrary to the idea that the  $^3\text{He}$  plume is produced at the spreading center axis and transferred into the distant site to the west, since the sites SA-6 and SA-7 are located further from the East Pacific Rise than GEOSECS sites 251 and 263. There may be another source of mantle derived helium close to the sites SA-6 and SA-7 such as submarine volcanism related to subduction (Sano et al., 1995). This is not explored further here, as it is not the principle objective of this study.

#### IV. Time rate of atmospheric $^3\text{He}/^4\text{He}$ change

In a recent paper, Sano et al. (1989) reported a decrease of 0.078%/year in the atmospheric  $^3\text{He}/^4\text{He}$  ratio based on helium isotope measurements of 20 air samples collected at various sites in Japan and in California during the period from 1977 to 1988. The decrease was attributed to an anthropogenic release of crustal helium from oil and natural gas wells. Lupton and Graham (1991) reported that the data of Sano et al. (1989) do not show a decrease with time based on statistical treatment. To add credence to their argument, Lupton and Graham (1991) has measured the  $^3\text{He}/^4\text{He}$  ratios of six California marine air collected in 1973, 1980s, 1990 and 1991 and presented the time rate of atmospheric  $^3\text{He}/^4\text{He}$  change of  $-0.0074 \pm 0.0372\%$ /year ( $2\sigma$ ). They also gave the time rate of  $-0.0067 \pm 0.1400\%$ /year ( $2\sigma$ ) based on the three independent measurements of absolute air  $^3\text{He}/^4\text{He}$  ratio, which is again consistent with zero time rate at the 95% confidence level (Lupton and Graham, 1991). They concluded no temporal changes in atmospheric  $^3\text{He}/^4\text{He}$  ratios outside the analytical precision.

In reply to Lupton and Graham (1991), Sano et al. (1991) recalculated statistically the data of air  $^3\text{He}/^4\text{He}$  ratios published in Sano et al. (1989) and provided the time rate of  $-0.081 \pm 0.062\%$ /year ( $2\sigma$ ). The time rate is consistent with that of the three independent measurements, but is not mostly compatible with data by Lupton and Graham (1991). Hoffman and Nier (1993) reported the absolute helium isotope ratio which was determined in 1956 at the University of Minnesota. They claimed that the time rate of atmospheric  $^3\text{He}/^4\text{He}$  change is  $-0.027 \pm 0.870\%$ /year and there is not any decrease in the atmospheric  $^3\text{He}/^4\text{He}$  ratio during a 32 year period. On the other hand, Sano (1993) suggested that the most reliable estimate for the rate of decrease of the atmospheric  $^3\text{He}/^4\text{He}$  ratio is  $0.032 \pm 0.013\%$ /year ( $2\sigma$ ) based on possible anthropogenic release of crustal helium from oil and natural gas wells and common value of three independent estimations, which are three absolute determinations (Lupton and Graham, 1991; Sano et al., 1991). Thus the problem is still controversial.

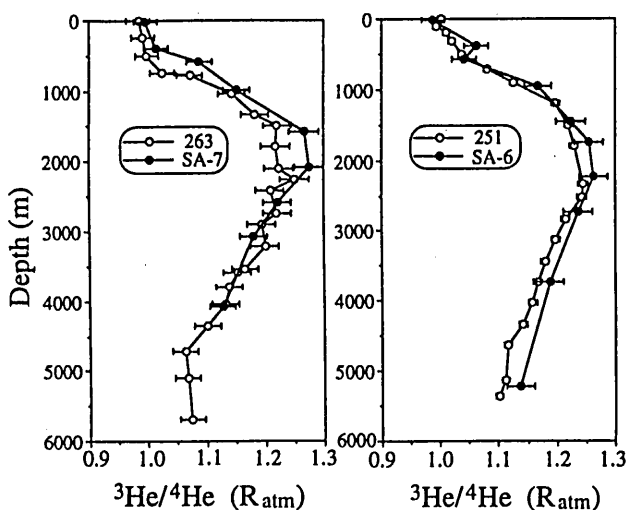


Figure 1. Excess  $^3\text{He}$  profiles at sites SA-7 and 263 and those at sites SA-6 and 251 in the South Pacific Ocean (Sano et al., 1995). The  $^3\text{He}/^4\text{He}$  ratios of sites SA-7 and SA-6 are calibrated against atmospheric helium collected in Chiba, Japan in August 1992 and those of 263 and 251 against air in California, 1972.

It is noted that the  $^3\text{He}$  residence time is about 4000 years in the deep ocean (Lupton and Craig, 1981) and based on the carbon-14 measurements deep seawater has been isolated from the present atmosphere for at least 1500 years (Ostlund et al., 1987). Since the vertical movement of helium in the ocean is significantly smaller than that of horizontal way by the eddy diffusion, the  $^3\text{He}$  plume should be preserved in some places 1000 km distant from the spreading center axis on the East Pacific Rise. GEOSECS Pacific Expedition data (Ostlund et al., 1987) suggested that movement of helium along the latitude (east to west) is more rapid than across the latitude (south to north) in the ocean. Thus the  $^3\text{He}$  excesses observed at sites SA-6 and SA-7 should be compatible with those reported at GEOSECS sites 251 and 263 with their

Table 2. Helium isotope ratios of South Pacific Deep Seawater samples and the estimated time rate of atmospheric  $^3\text{He}/^4\text{He}$  change.

	SA-7#	263*	SA-6#	251*
Pacific water				
Location	14°16'S, 154°19'E	16°41'S, 167°3'W	6°38'S, 153°38'E	4°34'S, 179°0'E
Depth (m)	2083	2254	2234	2332
$^3\text{He}/^4\text{He}$ ( $R_{\text{SPDW}}/R_{\text{atm}}$ )	1.276±0.026	1.250±0.025	1.263±0.025	1.244±0.007
Reference air				
Date	August 1992	1973	August 1992	1973
Location	Chiba, Japan	California, USA	Chiba, Japan	California, USA
$^3\text{He}/^4\text{He}$ ( $R_{\text{atm}}/R_{\text{SPDW}}$ )	0.7837±0.0157	0.8000±0.0160	0.7918±0.0158	0.8039±0.0048
Time rate of atmospheric $^3\text{He}/^4\text{He}$ change				
	-0.1072±0.2084 %/year		-0.0796±0.1087 %/year	

\*: Data from Ostlund et al. (1987)

#: Data from Sano et al. (1995)

Error assigned to the ratio is  $2\sigma$ .

## V. Constraint from South Pacific deep seawater

As is described above, observed peak  $^3\text{He}/^4\text{He}$  ratios of South Pacific deep seawater are higher than those expected by GEOSECS Pacific Expedition (Fig. 1). This may be attributable to an experimental artifact. GEOSECS data is calibrated against the California marine air collected in 1973 (Lupton and Graham, 1991) and data of Sano et al. (1995) against the Chiba air in Japan in August 1992. If the South Pacific deep seawater has identical  $^3\text{He}/^4\text{He}$  ratios between Hakuho Maru sites SA-6 and SA-7 and GEOSECS sites 251 and 263, the atmospheric  $^3\text{He}/^4\text{He}$  ratio to which seawater samples were calibrated, is variable. Thus the  $^3\text{He}/^4\text{He}$  ratios of seawater samples may help resolve the debate over the rate at which atmospheric  $^3\text{He}/^4\text{He}$  may be changing.

Table 2 lists the comparison of peak  $^3\text{He}/^4\text{He}$  ratios of South Pacific deep seawater with the depth between 1500 m and 3000 m. The  $^3\text{He}/^4\text{He}$  data are expressed as  $R_{\text{clf}}/R_{\text{spdw}}$  or  $R_{\text{chb}}/R_{\text{spdw}}$  where  $R_{\text{clf}}$ ,  $R_{\text{spdw}}$  and  $R_{\text{chb}}$  denote the  $^3\text{He}/^4\text{He}$  ratios of California air, South Pacific deep seawater, and Chiba air, respectively. Samples shallower than 1500 m are not used since they may be affected by a subduction of surface seawater with a tritium-decay. Samples deeper than 3000 m are also excluded because they may be compromised by the topography of the sea bottom. Table 2 also indicates the estimated time rates of  $^3\text{He}/^4\text{He}$  change based on the seawater samples and the time difference of California air collected in 1973 and Chiba air in August 1992. Errors assigned to the rates are  $2\sigma$  values. It is noted that the time rates are derived under the assumption that the excess  $^3\text{He}$  in Hakuho Maru samples is identical to that of GEOSECS samples. Actually

the former excess  $^3\text{He}$  may be smaller than that of the latter, since the former sites are located more distant from the spreading center axis on the East Pacific Rise and the excess

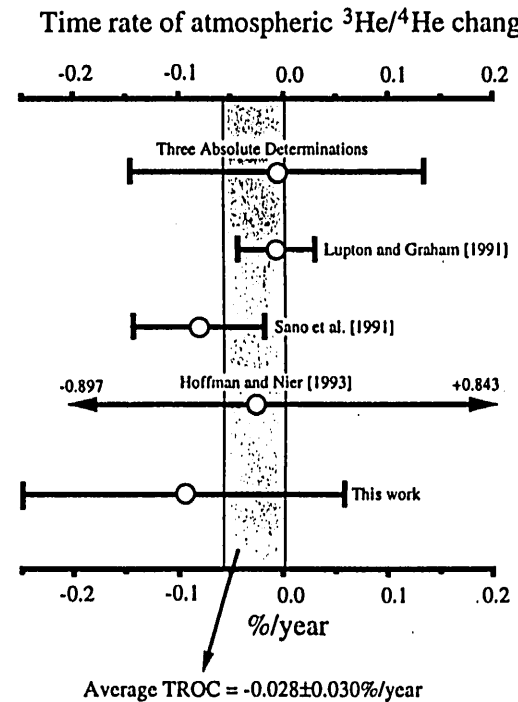


Figure 2. Time rate of atmospheric  $^3\text{He}/^4\text{He}$  change estimated in this work compared with literature data. Shadow shows average time rate of atmospheric  $^3\text{He}/^4\text{He}$  change calculated from five independent determinations.

$^3\text{He}$  may be lowered by a diffusive loss in Hakuho Maru samples. This means that estimated time rates in Table 2 are the lower limit in the case. Anyway both data sets of the rate are consistent with zero rate of change in atmospheric  $^3\text{He}/^4\text{He}$  ratio at the 95% confidence level.

Average of the seven estimations by South Pacific deep seawater are  $-0.094 \pm 0.156$  %/year ( $2\sigma$ ), when taking into account the weight of the error. Figure 2 summarizes the time rate of atmospheric  $^3\text{He}/^4\text{He}$  change obtained in this work and so far reported four data sets for the purpose of comparison. The time rate of Hoffman and Nier (1993) has a large error margin and thus agrees with all the other estimates within  $2\sigma$ . The time rate of this work is consistent with both Lupton and Graham (1991) and Sano et al. (1991) within  $2\sigma$  error margin. Average of the five determinations is  $-0.028 \pm 0.030$  %/year ( $2\sigma$ ), when taking into account the weight of each error. This is again consistent with zero rate of change in atmospheric  $^3\text{He}/^4\text{He}$  ratio at the 95% confidence level.

## VI. Constraint from anthropogenic release of crustal helium

Several sources of the anthropogenic helium were examined by Sano (1993). Table 3 lists possible source and sink of atmospheric helium. Grade-A helium production for cryogenic technology, welding and space missions was well documented with the rate of  $2.4 \times 10^9$  mole helium/year (Leachman, 1987). I calculate helium flux due to natural gas and oil exploitation based on their annual production rate in the literature and the estimated helium/carbon ratio. Assuming that the helium/carbon ratio is  $2 \times 10^{-3}$  (Oliver et al., 1984; Zartman et al., 1961), natural gas production in the world of  $8.6 \times 10^{13}$  mole carbon/year (Oil and Gas Journal, 1988) yields the flux of  $1.7 \times 10^{11}$  mole helium/year.

It is rather difficult to estimate the helium/carbon ratio of petroleum. Crude oil is usually accompanied by methane-rich gas. Helium prefers the gas phase to liquid, and it may be concentrated in the methane-rich gas from oil. Literature value of annual production takes into account only liquid phase of petroleum, and the total amount of gas flared or vented at well heads is not well documented. Vassoevich et al. (1967) estimated that oil reservoirs in the worldwide contain two or three times as much oil as gas. Assuming that the oil/gas ratio is three and the helium/carbon ratio of  $2 \times 10^{-3}$  in the gas phase, petroleum production in the world of  $1.9 \times 10^{14}$  mole carbon/year (Oil and Gas Journal, 1988) yields the flux of  $1.3 \times 10^{11}$  mole helium/year. This is compatible with helium flux from the natural gas production. Helium flux from coal mine ventilation and by degassing of coal is estimated  $4.4 \times 10^9$  mole helium/year by the global emission of methane from coal mines (Cicerone and Oremland, 1988) and a helium/carbon ratio of  $2 \times 10^{-3}$ . Thus the sum of

Table 3. Possible source and sink of atmospheric helium

	He (mole/year)
<i>Total inventory</i>	$9.3 \times 10^{14}$ mole (a)
<i>Source</i>	
Natural flux	
Degassing of solid Earth	$6.1 \times 10^8$ (a)
Fossil fuel flux	
Grade-A Helium Production	$2.4 \times 10^9$ (b)
Natural Gas Production	$1.7 \times 10^{11}$
Petroleum Production	$1.3 \times 10^{11}$
Coal Production	$4.4 \times 10^9$
Total	$3.1 \times 10^{11}$
<i>Sink</i>	
Escape (Thermal and Non-thermal)	$8.3 \times 10^8$ (a)

(a): Data from Ozima and Podosek (1983)

(b): Data from Leachman (1987)

anthropogenic helium fluxes is  $3.1 \times 10^{11}$  mol/year.

Taking into account the total inventory of helium of  $9.3 \times 10^{14}$  mole in the atmosphere and assuming that the crustal helium has the  $^3\text{He}/^4\text{He}$  ratio of  $3 \times 10^{-8}$ , I estimate the time rate of atmospheric  $^3\text{He}/^4\text{He}$  decrease of 0.033%/year based on the anthropogenic emission of crustal helium. The value of  $-0.033$  %/year agrees well with  $-0.028 \pm 0.030$  %/year obtained by the average of the five determinations as stated above. Therefore the problem of time rate of atmospheric  $^3\text{He}/^4\text{He}$  change is not solved and there is a pressing need and basis for (e.g.) NIST to establish helium isotopic standards which can be distributed and made available to noble gas laboratories in the world.

## VII. Conclusion

I have reviewed the possible time rate of atmospheric  $^3\text{He}/^4\text{He}$  change based on the helium isotope ratios of South Pacific deep seawater. The estimated rate of  $-0.094 \pm 0.156$  %/year ( $2\sigma$  error) is consistent with a zero rate of change. The average time rate of  $-0.028 \pm 0.030$  %/year ( $2\sigma$ ) by five independent researches including this work is again compatible with a zero rate of change. However the average time rate agrees well with the time rate of  $-0.033$  %/year estimated from anthropogenic release of crustal helium with low  $^3\text{He}/^4\text{He}$  ratio. Thus further study is desirable in order to settle the problem.

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