Jour. Sci. Hiroshima Univ., Ser. C, Vol. 9, No. 4, 597–602 (1993)

Time rate of atmospheric $^3He/^4He$ change: An attempt to measure anthropogenic CO_2 flux

By

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with 1 Table and 1 Figure

(received, December 25, 1992)

Abstract: Taking into account recently published data, the author assesses possible time rate change of atmospheric $^3He/^4He$ ratio. Three independent estimations are considered and the common value of the $^3He/^4He$ variations is proposed. The most reliable decreasing rate of atmospheric $^3He/^4He$ ratio, 0.032 ± 0.013 %/year is consistent with the anthropogenic emission of crustal helium of 3.1×10^{11} mol/year estimated by the statistics of global fossil fuel exploitation and the probable carbon/helium ratio in the fuel. Because of the inert chemistry of helium, atmospheric $^3He/^4He$ change may provide a marker against which to calibrate the absolute flux and retention of anthropogenic CO_2 in the atmosphere.

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I. Introduction

Since the Industrial Revolution, atmospheric CO_2 has increased apparently due to human activity (Keeling et al., 1976; Neftel et al., 1985). The Earth's climate is dependent upon the radiative balance of the atmosphere, and therefore upon the increase of greenhouse gases such as CO_2, N_2 and CH_4. The enhancement of atmospheric CO_2 should affect the global climate (Broecker, 1975). Although mass balance of CO_2 in the air has been a major subject of debate for Earth and Environmental scientists, the source and the sink of anthropogenic CO_2 are not well understood. The observed rise of CO_2 concentration in the atmosphere could be attributed to combustion of fossil fuels (Damon et al., 1973). Tropical deforestation may be another contributor (Woodwell et al., 1978). Terrestrial ecologists considered that the latter component was significant in the atmospheric CO_2 budget (Siegenthaler and Oeschger, 1987), while geophysicist reported that the global deforestation was not the major source of atmospheric CO_2 (Tans et al., 1990). The uptake of CO_2 by the oceans was estimated to be a value between 26 % and 44 % of the fossil CO_2 emission (Broecker et al.,

1979; Toggweiler et al., 1989; Tans et al., 1990). It was derived from computational calculations based on oceanographical models and fluid dynamics and is still significantly uncertain.

The terrestrial air contains helium with a concentration of 5.24 ppm by volume (Glückauf, 1946). Helium is escaping from the high temperature exsosphere to inter-planetary space because of its light mass (Kockerts and Nicolet, 1962). Helium is supplied by the solid Earth through volcanic activity (Craig et al., 1975) and fault movement (Tugarinov et al., 1975). There may be an approximate balance between escape flux from the atmosphere and degassing from the mantle and crust (Sano, 1986; Torgersen, 1989). It is well documented that petroleum and natural gases contain appreciable amount of helium (Zartman et al., 1961). Fossil fuel exploitation may have some effects on the mass balance of helium in the air as does fuel combustion on the CO_2 budget. On the other hand, the global deforestation could not have any relation to the helium budget since the element is chemically inert. Temporal change of helium content in the air may provide important constraints on the atmospheric CO_2 budget. There is, however, no reliable datum in literature. This is partly due to difficulty of precise measurement of absolute helium content in the air. Taking into account recent data of helium isotope ratio, the author assesses the temporal change of helium content and discusses the flux and retention of anthropogenic CO_2 in the atmosphere.

Acknowledgements

The author is grateful to Drs. G. Igarashi and M. Watanabe for their comments and suggestions. This paper was reviewed by Dr. S. Sasaki.

II. Atmospheric helium isotope ratios

Helium has two stable isotopes of mass number 3 and 4. Terrestrial ^3He is believed to be derived from the upper mantle by volcanic activity (Craig et al., 1975), while most ^4He is generated by radioactive decay of U and Th in crustal rocks (Morrison and Pine, 1955). There are two natural sources of atmospheric helium. One is crustal helium with the $^3He/^4He$ ratio of about $2x10^{-8}$ and another is mantle derived helium with the ratio of about $1x10^{-5}$. The isotope ratio of atmospheric helium was believed to be constant on a global scale since the mixing time for mantle and crustal helium in the atmosphere was significantly shorter than the residence time for helium (Lupton, 1983). Thus air helium has been used as a calibrating standard gas sample for noble gas mass spectrometry at almost all laboratories in the world.

There were only two precise $^3He/^4He$ measurements of atmospheric helium before 1985. Mamyrin et al. (1970) determined the air $^3He/^4He$ ratio of $(1.399\pm0.013)x10^{-6}$ in Leningrad (USSR). Clarke et al. (1976) reported that the $^3He/^4He$ ratio of air helium in Ontario (Canada) was $(1.384\pm0.006)x10^{-6}$. An average of the two isotope measurements, $(1.39\pm0.01)x10^{-6}$ was generally accepted as the atmospheric $^3He/^4He$ ratio (Lupton, 1983). Recently Sano et al. (1988) observed atmospheric $^3He/^4He$ ratio of $(1.343\pm0.013)x10^{-6}$ at Ueno Park, central Tokyo (Japan). The recent value was apparently lower than the previous data. Either experimental artifacts or a natural phenomenon was taken into account.

III. Time rate of air helium isotope change

If three independent analyses of air $^3He/^4He$ ratio are experimentally correct, there may be a decreasing trend of the $^3He/^4He$ ratio at the rate of $(3.0\pm0.9)x10^{-9}$/year. In order to check the variation, Sano et al. (1989) measured helium isotope ratios in old air samples which were collected for the purpose of monitoring atmospheric halocarbons and has been stored in a stainless-steel canister. A change in the atmospheric $^3He/^4He$ ratio from $1.362x10^{-6}$ in December 1977 to $1.339x10^{-6}$ in September 1988, or a decrease of about $1x10^{-9}$/year was found. Although the rate of change is smaller than the estimation by three independent analysis, a decreasing trend of atmospheric $^3He/^4He$ ratio was verified.

Recently Lupton and Graham (1991) claimed that data of Sano et al. (1989) was not statistically different from a zero time rate of change. They stated that a linear regression fit to three absolute $^3He/^4He$ determinations of air helium (Mamyrin et al., 1970; Clarke et al., 1975; Davidson and Emerson, 1990) yielded a slope of a zero rate of change, $-0.0067\pm0.14\%$/year (2σ error), although they neglected an absolute measurement by Sano et al. (1988) in their calculation. Lupton and Graham (1991) also presented California marine air data which showed no evidence of $^3He/^4He$ variation with time, whose rate was $0.0093\pm0.043\%$/year (2σ error). Then Sano et al. (1991) recalculated a decreasing rate of atmospheric $^3He/^4He$ ratio of $-0.081\pm0.062\%$/year (2σ error) and concluded that the time rate of atmospheric $^3He/^4He$ change could be statistically different from a zero. After papers by Lupton and Graham (1991) and Sano et al. (1991) were accepted for publication, Lupton and Graham (1991) performed the additional analyses and reported in notes added in proof that a time rate of $^3He/^4He$ change of -0.0074 ± 0.0372 %/year (2σ error) was consistent with a zero time rate of change.

A decrease in the atmospheric helium isotope ratio has serious implications for the field of noble gas isotope geochemistry. Controversy of the time rates of $^3He/^4He$ change (TROC) should be resolved. Figure 1 shows a comparison of three independent data sets so far reported (Absolute determinations; Lupton and Graham, 1991; Sano et al., 1991). Bars indicates uncertainty of TROC measurements by 2σ error. Although exact TROC value by Sano et al. (1991) is apparently different from those by absolute determinations and Lupton and Graham (1991), three independent determinations agrees well at values between -0.045 %/year and -0.019 %/year when one takes into account the 2σ error. Thus the common TROC gives us the atmospheric $^3He/^4He$ change of

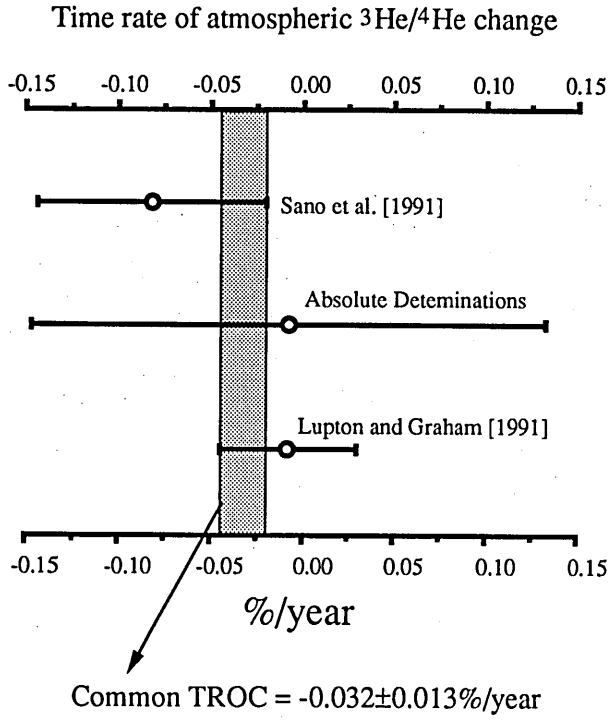

Figure 1. Comparison among three independent determinations of time rate of $^3He/^4He$ change (TROC). A hatched zone shows common TROC of -0.032±0.013%/year. Note that simple average of the three yields 0.0317%/yeat. Bars indicate uncertainty of determination by 95% confidential interval.

-0.032±0.013 %/year at the 95% confidence interval. It is noted that simple arithmetic average of three TROCs is -0.0317 %/year, again agrees well with the common TROC. Since these TROCs were obtained by independent experiments, the common value would be a reliable $^3He/^4He$ change in the air.

IV. Anthropogenic release of crustal helium

The estimated decrease of atmospheric $^3He/^4He$ ratio may be attributed to several natural phenomena such as decrease in solar activity and that in global volcanic activity, or non-steady state atmosphere for helium (Sano et al., 1989). It is, however, difficult assess the effects quantitatively. Anthropogenic release of crustal helium with low $^3He/^4He$ ratio may be another candidate to explain the common TROC. Furthermore this may provide important constraints on the atmospheric CO_2 budget since helium and carbon have a similar source. If the decrease of atmospheric $^3He/^4He$ ratio is caused by anthropogenic release of crustal helium with the ratio of $3x10^{-8}$, it is possible to calculate the time rate. The estimated rate is $(3.0\pm1.3)x10^{11}$ mole He/year, which is about 500 times larger than natural degassing flux of $6.1x10^8$ mole He/year from the solid Earth (Ozima and Podosek, 1983).

Probable sources of the anthropogenic helium should be examined. Table 1 summarizes possible source and sink of atmospheric helium. Grade-A helium production for cryogenic technology, welding and space mission was well documented (Leachman, 1987). The rate of $2.4x10^9$ mole He/year is significantly smaller than the rate estimated by common TROC. One can calculate helium flux due to natural gas and petroleum exploitations based on their annual production rate in literatures and estimated helium/carbon ratio. Assuming that the helium/carbon ratio is $2x10^{-3}$ (Zartman et al., 1961; Oliver et al., 1984), natural gas production in the world of 8.6×10^{13} mole C/year (Oil and Gas journal, 1988) yields the flux of $1.7x10^{11}$ mole He/year, which is about half of the rate by common TROC.

It is difficult to estimate the helium/carbon ratio of petroleum. Crude oil is usually accompanied with methane-rich gas in the occurrence. Helium prefers gas phase to liquid. Literature value of annual production takes into account only liquid phase, and the total amount of gas flared or vented at well head is not documented, even though helium should be incorporated in the gas. Vassoevich et al. (1967) estimated that oil reservoirs worldwide contain two or three times as much oil as gas. Assuming that the oil/gas ratio is 3 and the helium/carbon ratio of $2x10^{-3}$ in the gas phase, petroleum production in the world of $1.9x10^{14}$ mole C/year (Oil and Gas journal, 1988) yields the flux of $1.3x10^{11}$ mole He/year. The value is compatible with helium flux from natural gas.

Methane is released to the atmosphere by coal mine ventilation and by degassing from coal during transport. Global emission from coal mining was estimated to be $2.2x10^{12}$ mole C/year (Cicerone and Oremland, 1988). Again assuming the helium/carbon ratio of $2x10^{-3}$, one can obtain the flux of $4.4x10^9$ mole He/year. Then sum of fossil fuel helium fluxes is $3.1x10^{11}$ mole/year, which may have an uncertainty of

Table 1. Possible souce and sink of atmospheric helium and CO_2

Item	^4He (mole/year)	CO_2 (mole/year)
Total inventory		
	$9.3x10^{14}$ mole (a)	$6.3x10^{16}$ mole (g)
Source		
Natural flux		
Degassing of solid Earth	6.1×10^8 (a)	2.0×10^{12} (b)
Fossil fuel flux		
Grade-A Helium Production	2.4×10^9 (c)	0 (d)
Natural Gas Production	1.7×10^{11} (d)	8.6×10^{13} (e)
Petroleum Production	1.3×10^{11} (d)	1.9×10^{14} (e)
Coal Production	4.4×10^9 (d)	2.4×10^{14} (f)
Total	3.1×10^{11} (d)	5.2×10^{14} (d)
Deforestation	0 (d)	$(1.3\pm0.8)x10^{14}$ (g)
Sink		
Escape (Thermal and Nonthermal)	8.3×10^8 (a)	0 (d)
Oceanic Uptake	0 (d)	$(1.7\pm0.7)10^{14}$ (g)
Atmospheric increase		
	$3.0\pm1.3x\ 10^{11}$ (d)	3.2×10^{14} (g)

(a) Ozima and Podosek (1983); (b) Marty and Jambon (1987); (c) Leachman (1987); (d) This work; (e) Oil and Gas Journal (1988); (f) Coal Report (1991); (g); Watson et al. (1990)

±30% caused by ambiguity of oil/gas ratio in oil reservoirs. This value agrees well with atmospheric increase of $(3.0\pm1.3)x10^{11}$ mole He/year estimated by common TROC.

V. Implications for anthropogenic carbon flux

Recent estimation of atmospheric CO_2 budget is shown in Table 1 together with helium budget. There is an approximate balance between source and sink of atmospheric helium, that is, anthropogenic helium flux is equivalent to the atmospheric increase. In contrast, there is not a balance between source and sink of atmospheric CO_2. Anthropogenic CO_2 flux exceeds the sum of oceanic uptake and atmospheric increase. This is called "missing sink" of atmospheric CO_2. It is interesting to evaluate each source and sink of CO_2 based on helium budget. Atmospheric balances of helium and CO_2 are described as follows:

$$(He)_{fuel} = (He)_{increase}$$
$$(CO_2)_{fuel} + (CO_2)_{deforest} - (CO_2)_{ocean} = (CO_2)_{increase}$$

where subscript fuel, deforest, ocean and increase denote flux of the species by fossil fuel, deforestation and oceanic uptake, and atmospheric increase, respectively. Natural fluxes of helium and CO_2 from the solid Earth are not taken into account in the equations, since they have far small figures (Ozima and Podosek, 1983; Marty and Jambon, 1987). Agreement of helium flux between fossil fuel and atmospheric increase suggests that the petroleum, natural gas and coal which were exploited, can be fully consumed by human activity. This means that total production of fossil fuel is equivalent to the amount of combustion and this rules out possibility of significant storage of fossil fuel. Thus total CO_2 flux of $5.2x10^{14}$ mole/year by fossil fuel production is a reliable estimate.

Atmospheric CO_2 increase of $3.2x10^{14}$ mole/year is an observational result (Watson et al., 1990) and there is not large ambiguity in it. The "missing sink" can be caused by errors of CO_2 flux by deforestation and oceanic uptake. The atmospheric CO_2 budget is modified as follows:

$$(CO_2)_{ocean} - (CO_2)_{deforest} =$$
$$(CO_2)_{fuel} - (CO_2)_{increase} = 1.9x10^{14} \text{ mole/year}$$

where uncertainty of difference between fossil fuel flux and atmospheric increase, $2.0x10^{14}$ mole/year, is significantly small as stated above. It is certain that deforestation have no relation to the helium budget. Oceanic uptake does not contribute to helium budget as well, since solubility of the element is significantly small (Ozima and Podosek, 1983). Thus it is not probable to verify CO_2 flux by deforestation and oceanic uptake based on the helium budget only. In other words, decrease of atmopsheric $^3He/^4He$ ratio

does not give constraints on CO_2 flux by deforestation and oceanic uptake.

If one takes the maximum estimate for oceanic uptake, 2.4×10^{14} mole/year and the minimum for deforestation, 5×10^{13} mole/year (Watson et al., 1990), atmospheric CO_2 budget can be scarcely balanced. This idea is compatible with a model of geophysicist (Tans et al., 1990). Further study is highly desirable to provide rigid constraint on CO_2 flux by deforestation and oceanic uptake. We should search chemical element or species, which is released from fossil fuel and is absorbed in ocean but have no relation to deforestation, or which is released from deforestation but is not absorbed in ocean.

In conclusion, the common TROC provides the atmospheric $^3He/^4He$ change of -0.032 ± 0.013 %/year at the 95% confidence interval. The decrease can be attributed to anthropogenic release of crustal helium with low $^3He/^4He$ ratio. Since helium and carbon have similar source such as natural gas and petroleum, it is possible to verify CO_2 flux by fossil fuel production. In order to balance atmospheric CO_2 budget, one can consider the maximum estimate for oceanic uptake flux and the minimum for deforestation flux.

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