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► To cite this version:

J Mabry, Tf Lan, C Boucher, Christine Boucher, P.G. Burnard, et al.. No evidence for change of the atmospheric helium isotope composition since 1978 from re-analysis of the Cape Grim Air Archive. Earth and Planetary Science Letters, 2015, 10.1016/j.epsl.2015.07.035 . hal-01346175

HAL Id: hal-01346175

<https://hal.science/hal-01346175>

Submitted on 22 Jul 2016

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No evidence for change of the atmospheric helium isotope composition since 1978 from re-analysis of the Cape Grim Air Archive

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Abstract

The helium isotope composition of air might have changed since the industrial revolution due to the release of ^4He -rich crustal helium during exploitation of fossil fuels. Thereby, variation of the atmospheric helium isotope ratio ($^3\text{He}/^4\text{He}$) has been proposed as a possible new atmospheric tracer of industrial activity. However, the magnitude of such change is debated, with possible values ranging from 0 to about 2‰/yr (Sano, 1989; Hoffmann and Nier, 1993; Pierson-Wickmann et al., 2001; Brennwald et al., 2013; Lupton and Evans, 2013). A new analytical facility for high precision (2‰, 2σ) analysis of the $^3\text{He}/^4\text{He}$ ratio of air has been developed at CRPG Nancy (France) capable of investigating permil level variations. Previously, Brennwald et al. (2013) analyzed a selection of air samples archived since 1978 at Cape Grim, Tasmania, by the Commonwealth Scientific and Industrial Research Organisation (CSIRO). They reported a mean temporal decrease of the $^3\text{He}/^4\text{He}$ ratio of 0.23-0.30‰/yr. Re-analysis of aliquots of the same samples using the new high-precision instrument showed no significant temporal decrease of the $^3\text{He}/^4\text{He}$ ratio (0.0095 ± 0.033 ‰/yr, 2σ) in the time interval 1978-2011. These new data

constrain the mean He content of globally produced natural gas to about 0.034% or less, which is about 3× lower than commonly quoted.

Introduction

The helium isotopic composition of air may be able to provide a new tracer for studying and quantifying environmental changes resulting from global warming and anthropogenic activity. Due to their light masses, the two isotopes of helium escape to space through thermal and non-thermal processes (Ozima and Podosek, 2002). Consequently, the helium content of air is low (5.24 ppm vol., Gluckauf, 1946) and the atmospheric He isotope ratio is a transient value determined by variations of the strengths of sources (outgassing of the solid earth, extraterrestrial contributions) and sinks (loss to space) of ^3He and of ^4He over time (Ozima and Podosek, 2002). The He isotope residence time in the atmosphere is of the order of 10^4 - 10^6 yr (Torgersen, 1989; Kockarts, 1973), much longer than the atmospheric mixing time of 10 yr. Thus, the $^3\text{He}/^4\text{He}$ ratio of modern air (1.34 - 1.40×10^{-6} , Mamyrin et al., 1969; Clarke et al., 1975; Davidson et al., 1988; Hoffmann and Nier, 1993; Sano et al., 1988) should be constant on a decadal timescale. However, it has been suggested that

61 this may no longer be the case (Sano, 1989; Pierson-Wickmann et al.,
62 2001; Brennwald et al., 2013; Lupton and Evans, 2013).

63 The exploitation of fossil fuels (coal, liquid and gaseous
64 hydrocarbons) may have released large amounts of ^4He during the
65 past couple of centuries and particularly the last few decades as
66 natural gas production has more than doubled between 1971 and
67 2012 (IEA, 2014). The recent rapid release of gases from these
68 reservoirs, which have concentrated crustal helium for tens to
69 hundreds of Ma, could have decreased the $^3\text{He}/^4\text{He}$ in the atmosphere
70 (Sano, 1989; Pierson-Wickmann et al., 2001; Brennwald et al., 2013).
71 Other anthropogenic extraction industries such as mining or quarrying
72 may also liberate unknown quantities of radiogenic He into the
73 atmosphere (Sano, 2010).

74 The only potential anthropogenic source of excess ^3He that could
75 increase the atmospheric $^3\text{He}/^4\text{He}$ ratio is He produced during induced
76 U or Pu fission either in nuclear reactors or in nuclear weapons
77 (Lupton and Evans, 2004). However, anthropogenic nuclear He
78 sources can be relatively well quantified and do not contribute
79 significant He to the atmosphere (Lupton and Evans, 2004).

80 Studies on the atmospheric helium variations, summarized in
81 Brennwald et al. (2013) (e.g., compilation in their Table 1), resulted in

contradictory results, indicating either decreases in the $^3\text{He}/^4\text{He}$ ratio of the order of 0.1-0.3 ‰/yr during the last few decades (Sano et al., 2010; Matsuda et al., 2010), or no detectable change since at least 1973 (Lupton and Evans, 2013) or possibly 1956 (Hoffmann and Nier, 1993).

The study of Brennwald et al. (2013) is particularly relevant, because it presents results of temporal atmospheric helium variations from samples periodically archived in stainless steel containers since 1978 (Cape Grim Air Archive (CGAA), Tasmania; Langenfelds et al., 1996). As these samples were collected from a single location, Brennwald et al. (2013) argued that potential problems due to geographical heterogeneities should not apply. Based on a statistical analysis of repeated runs, Brennwald et al. reported a mean decrease of the $^3\text{He}/^4\text{He}$ ratio of 0.23 to 0.30 ‰/yr during this period of time. In contrast, Lupton and Evans (2013) did not observe any significant difference between $^3\text{He}/^4\text{He}$ ratios measured in air samples taken at a single location (La Jolla, California, USA) in 1973 and 2013. Together with other data from different locations and periods of time, they derived a mean rate of decrease of the $^3\text{He}/^4\text{He}$ ratio of $(0.014 \pm 0.045)\text{‰/yr}$ (2σ), which is consistent with zero rate of change over a 40-year period.

We have developed a dedicated facility at CRPG Nancy (France) that permits the analysis of the $^3\text{He}/^4\text{He}$ ratio of air with a precision for individual measurements of about 2‰ (2σ , Mabry et al., 2014) which compares to about 14‰ (2σ , Brennwald et al., 2013). In order to further investigate and better constrain the results reported by Brennwald et al. (2013), we have analyzed aliquots of the same air samples from the CGAA, as well as 5 further samples from years not analyzed by Brennwald et al. (2013).

Method

The CGAA is a series of air samples collected typically every three months since 1978 at Cape Grim on the north-west tip of Tasmania. For each sample, 1-2 m³STP of air is collected and stored in 35-L stainless steel tanks. The sampling and storage conditions of the air samples were considered with great care to avoid pollution/contamination from cities and industry during sampling or modification of the sampled air during storage. This is necessary to provide a true baseline air sample for the southern hemisphere that could be used for many years. Details of the CGAA sampling procedure are documented in Langenfelds et al. (1996) and Brennwald et al. (2013).

Subsamples for $^3\text{He}/^4\text{He}$ analysis were chosen from a selection of ten archive tanks spanning the time period 1978 – 2011: 1978, 1979, 1984, 1988, 1993, 1997, 2000, 2004, 2008, 2011 (Table 1). Multiple subsamples were collected from each tank in 1.2-m-long, 3/8"-OD copper tubes, which were sealed by cold-welding with a crimping tool (Brennwald et al., 2013).

For measurement, a roughly 10 to 15 cm³ portion of the copper tube is sealed off with a steel clamp and attached to the extraction line using Swagelok Ultra-torr tube fittings and wrench-tightened. The sample manifold is then evacuated, the pump isolated, and the copper tube is opened to release the air sample into the extraction line for purification and then measurement. A full description of the sample processing and analysis is given in Mabry et al. (2013). Everything aside from helium and neon is removed from the sample gas using a series of getters and charcoal fingers. Then, the neon is separated from helium using a cryo trap so that only the helium remains to be admitted into the mass spectrometer. After purification of the sample, a series of eleven standard-bracketed measurements are made. The standard used for the bracketing measurements is derived from a purified air standard collected from the Brittany coast. Note that this standard He is enriched by 3.3% relative to the He isotope

composition of air, as a result of isotope fractionation during handling and purification of a large quantity of air. We attempted the purification procedure twice and obtained the same fractionation. The cause of this fractionation, possibly related to thermal effects between hot traps and traps at liquid N₂ temperature, are not fully elucidated. For our purpose however, the absolute value of the running standard has no bearing on the results (provided that its ³He/⁴He composition is close to that of air), because all samples are normalized to this common running standard and therefore can be inter-compared. In particular, we continuously calibrate atmospheric helium from local air (Brabois Park close to Nancy) against this standard (see below). Gas pressures of the purified sample aliquots are matched to within 2% of the standard aliquot pressures through the use of an adjustable volume in order to eliminate pressure effects in the mass spectrometer.

Additionally, local air sampled in a park near CRPG (Brabois Air) is analyzed periodically to compare all samples under the same analysis and sampling conditions, and so, to monitor the continued efficacy of the purification procedure and measurement stability. The measured ³He/⁴He values of Brabois Air samples were very stable (standard error 0.33 ‰, 2σ, N=83) over a year of measurements (Mabry et al.,

2013) over the same time period the CGAA sample measurements were made.

Results and Discussion

Helium in the Cape Grim Air Archive

In Table 1, we report measurements from a selection of copper-tube subsamples from the CGAA. Particular effort was made to make multiple measurements from the earliest (1978, 1979) and latest (2008, 2011) subsamples since these would be the most likely to show a detectable difference and would best constrain the trend over the time period.

Three of the data points are statistically significant outliers. The $^3\text{He}/^4\text{He}$ from 1988 and 2004 are 10-20‰ lower than all the other data points, while the $^3\text{He}/^4\text{He}$ ratio of the 1984 subsample is about 4‰ lower than in the other samples (excluding 1988 and 2004). A generalized extreme Studentized deviate (GESD) test (Appendix A, Rosner, 1983) confirms the 1988 and 2004 data points as outliers with 99% confidence whether the test is run using the ratios or the residuals of a best-fit linear time trend. This test assumes the dataset

is approximately normally distributed which we confirmed by a normal probability plot (not shown).

The 1984 tank at CSIRO is suspected of having a small leak as was noted in Brennwald et al. (2013). The nitrogen isotopes in this particular storage tank were detectably fractionated and additional testing showed a change in the relative concentrations of H₂, CH₄, CO₂, and N₂O over time (Brennwald et al., 2013). These indicate a small leak in this storage tank which would lead to a decrease in the ³He/⁴He over time as slightly more ³He effused out of the tank relative to ⁴He, consistent with our data showing a lower ³He/⁴He ratio relative to the other samples. We can correct for this effect using observed changes in the concentrations of H₂, CH₄, CO₂, and N₂O and Graham's Law to calculate the expected fractionation of the helium isotopes (as in Brennwald et al., 2013). The correction increases the 1984 ³He/⁴He by about 3.5‰, bringing it to well within the scatter of the rest of the data excluding 1988 and 2004 (Table 1). Neither the 1988 nor 2004 tanks at CSIRO show any evidence of leakage. Thus, it seems likely that these samples were fractionated at some point after subsampling, e.g., during storage or aliquoting of the subsamples. In the following discussion, we will consider both the uncorrected and effusion-corrected 1984 data but will exclude the 1988 and 2004 data.

Table 1: Helium isotope ratios from different subsamples of the Cape Grim Air Archive relative to our standard (R/Rstd) and then normalized to the overall mean of the data. Where more than one measurement was made, the error-weighted mean ($\bar{x}$) and the error of the mean is reported. Numbers in italics have been identified as statistical outliers.

Cape Grim Archive Tank	R/Rstd	2σ	Cape Grim Archive Tank	R/Rstd	2σ
7 Jul 1978 (UAN 780002)	1.0035	0.0020	2 Mar 1993 (UAN 930279)	1.0009	0.0021
	0.9992	0.0020			
	1.0026	0.0022	7 Jan 1997 (UAN 970008)	0.9989	0.0021
	0.9979	0.0024			
	$\bar{x}$ 1.0009	0.0011			
6 Feb 1979 (UAN 790001)	1.0015	0.0020	29 Sep 2000 (UAN 993562)	0.9988	0.0020
	1.0003	0.0022			
	1.0001	0.0021	1 Dec 2004 (UAN 997089)	0.9885	0.0019
	0.9992	0.0020			
	0.9997	0.0023			
	0.9979	0.0023	12 Aug 2008 (UAN 999756)	1.0001	0.0023
	0.9997	0.0024		1.0006	0.0022
	$\bar{x}$ 0.9999	0.0008		0.9994	0.0022
23 May 1984 (UAN 840004)	0.9963	0.0022	4 May 2011 (UAN 20110462)	$\bar{x}$ 1.0000	0.0013
	0.9963	0.0022		0.9990	0.0022
	$\bar{x}$ 0.9963	0.0016		0.9990	0.0020
Effusion corrected $\bar{x}$ 0.9997		0.0016		1.0007	0.0023
21 Jun 1988 (UAN 880003)	0.9783	0.0020		1.0017	0.0022
	0.9771	0.0032		$\bar{x}$ 1.0000	0.0011
	$\bar{x}$ 0.9780	0.0017			

An error-weighted least-squares fit (e.g. Baird, 1995) of the $^3\text{He}/^4\text{He}$ with the uncorrected 1984 ratio (excluding 1988 and 2004) results in a trend line with a slope that is essentially zero: $(0.000 \pm 0.033)\%$ /yr (2σ , Fig 1b). If the potential effusion effect on the $^3\text{He}/^4\text{He}$ value obtained from the 1984 tank is considered, the slope

216 corresponds to a $^3\text{He}/^4\text{He}$ decrease of $(0.0095 \pm 0.033)\text{‰/yr}$ (2σ ,
217 Fig 1b). The $^3\text{He}/^4\text{He}$ time series is therefore consistent with a constant
218 $^3\text{He}/^4\text{He}$ ratio and is constrained to a rate of decrease of less than
219 0.033‰/yr (2σ , assuming no effusion) or 0.042‰/yr (considering the
220 potential effusion effect of the 1984 tank) during 1978–2011.

221 This contrasts with the measurements of the CGGA reported by
222 Brennwald et al. (2013) of a decrease of $^3\text{He}/^4\text{He}$ during 1978–2011 of
223 $(0.23 - 0.30 \pm 0.16)\text{‰/yr}$ (2σ , Fig 1b). Although Brennwald et al. find
224 that their data are, in a statistical sense, more likely to be explained by
225 a linear decrease than by a constant $^3\text{He}/^4\text{He}$, their data does not rule
226 out the possibility of a constant $^3\text{He}/^4\text{He}$ per se. The new measurement
227 method used here yields much less scatter of the data for replicate
228 analyses of the same subsample as compared to those reported in
229 Brennwald et al. (Fig 1a). The data of this work and Brennwald et al.
230 do overlap at the 2σ -level (Fig 1b) and thus taken together are
231 consistent with no statistically significant change in the helium isotopes
232 of the Cape Grim Air Archive over the measured time period, but the
233 new data better constrain the upper limit of possible change.
234 Furthermore, this result is in good agreement with recently published
235 data by Lupton and Evans (2013), who report no significant change in

236 the helium isotopic ratio (Fig 1b) in air over the last few decades and a
237 maximum possible decrease of $^3\text{He}/^4\text{He}$ of 0.059‰/yr (2σ).

238 **Figure 1: (a)** The individual $^3\text{He}/^4\text{He}$ values from replicate analyses reported in Brennwald et al.
 239 2013 (solid circles) and those measured in this work (open squares). Data are normalized to the
 240 mean value of each respective data set to allow for direct comparison. **(b)** Shows the error-
 241 weighted means of the individual replicate measurements on subsamples. The effusion corrected
 242 1984 mean is shown with an open diamond. The error-weighted best-fit lines are shown for
 243 Brennwald et al. 2013 (dashed line), this work with 1984 effusion corrected (solid line) and
 244 uncorrected (dotted line). Also shown for comparison are data from Lupton and Evans (2013, solid
 245 triangles). All errors are 2σ .

246 Brennwald et al. (2013) also measured He/Ne ratios of the same
 247 samples and did not observe any significant trend if the uncorrected
 248 1984 data are excluded. If the change in helium isotopic ratio were due
 249 to excess ^4He released into the atmosphere as theorized, this should
 250 manifest also as an increasing He/Ne ratio over the same time period.
 251 The fact that they saw no change in this ratio was at odds with their
 252 helium isotope data, but is consistent with the new measurements in
 253 this work.

254 Helium in natural gas

255 The constancy of the $^3\text{He}/^4\text{He}$ ratio over the last few decades is
 256 inconsistent with available estimates for He isotope fluxes during this
 257 period, which predict a decrease of the $^3\text{He}/^4\text{He}$ ratio of about 0.1 %/yr

(Sano, 2010). These predictions are dependent on the global average He content of natural gas, which has been estimated to be 0.1-0.25% (Oliver et al., 1984). However, barring a credible source of excess ^3He , the data sets from this work and Lupton and Evans (2013) point to this being a significant overestimation of the mean helium content in natural gas produced globally.

These predicted He concentrations come primarily from the U.S. Bureau of Land Management's (previously Bureau of Mines) survey of natural gas compositions (see e.g BLM, 2008). A straight average of the helium compositions contained in this database yield an average helium content of around 0.25 – 0.3%. However, Lupton and Evans (2013) noted that this data shows an inverse correlation between helium content and reported production rate (open flow) of the well, indicating that there may be an inverse relationship between helium content and field size. Weighting the helium data by open flow brings the average down to around 0.15%. Additionally, this database may over-represent higher helium wells since it includes primarily data from U.S. wells (~16,700 U.S. records vs 133 non-U.S.) which may have a higher helium content than the rest of the world (non-U.S. average helium content ~ 0.06%). And this database may even over-sample higher helium wells within the U.S. as well since helium is an important

commodity. These factors suggest that the true average helium composition is likely less than 0.15%.

If we look directly at helium production, Mohr and Ward (2014) estimate that $\sim 2.0 \times 10^{11}$ moles were produced world wide between 1921 and 2012. Assuming most of this helium made its way into the atmosphere within a few years, it would lead to a decrease in the atmospheric $^3\text{He}/^4\text{He}$ of about 0.0025‰/yr (or about 0.225‰ over the 91-year span). Narrowing the focus to just the period 1978-2011, we have about 1.5×10^{11} moles produced world wide (U.S. Geological Survey, 2014), leading to a decrease in the atmospheric $^3\text{He}/^4\text{He}$ of about 0.005‰/yr (or about 0.15‰ over the 33-year span). If we further assume that helium is being extracted from most of the high-helium natural gas wells, then the average helium content for the remaining wells would be much lower. After accounting for helium production and using an average natural gas production over the last three decades of $\sim 1 \times 10^{14}$ mol/yr (IEA, 2014), then we find the average helium content of natural gas consistent with our data is at most 0.034% (2σ maximum). This is roughly 3 - 7× lower than the commonly quoted values of 0.1-0.25%.

Conclusion

We have re-analyzed the He isotope composition of a series of air aliquots sampled at Cape Grim, Tasmania, and stored in stainless steel taken by CSIRO. We do not observe any significant change in the $^3\text{He}/^4\text{He}$ ratio over this time period and find the maximum rate of decrease to be $0.033 - 0.042\text{‰/yr}$ (2σ); two outliers (1988 and 2004) have been excluded from the compilation. We do not reproduce the result of Brennwald et al. (2013), who, based on the analysis of air aliquots from the same series reported a decrease of $(0.23 - 0.30 \pm 0.16)\text{‰/yr}$ of the $^3\text{He}/^4\text{He}$ ratio between 1978 and 2011. Our results are consistent with previous reports that the He isotope composition of air has not changed by more than 0.059‰/yr (2σ) between 1973 and 2013 (Lupton and Evans, 2013), and with the results of Hoffmann and Nier (1993) who concluded there was no significant change in the $^3\text{He}/^4\text{He}$ ratio based on measurements done on air collected between 1956 and 1988. Our data suggests that the commonly reported mean concentration of helium in natural gas is significantly over-estimated (at least $3\times$) and is likely no more than 0.034% .

Given the inconsistency of reported atmospheric $^3\text{He}/^4\text{He}$ trends in the literature, the discrepancy in measurements of the same CGAA samples reported here and by Brennwald et al. (2013), and the unexplained fractionation of the 1988 and 2004 samples, it is proposed

that a new subset of CGAA samples should be prepared by CSIRO and analyzed at CRPG. These samples will be filled in stainless steel flasks with valves, rather than the copper tubes used previously, and will extend the time series to at least 2015.

Acknowledgments

This project has been funded by the French Agence Nationale de la Recherche (Project VIHA2) and by the European Research Council under the European Community's Seventh Framework Programme (FP7/2010-2016 grant agreement no. 267255). The Deep Carbon Observatory also provided funding support. We acknowledge the CSIRO and Cape Grim Baseline Air Pollution Station staff who assisted with collection, analysis and maintenance of the CGAA samples, and Dr. Paul Steele for helpful discussions relating to this work. Thanks also to helpful comments from two anonymous reviewers, and to Editor Derek Vance.

Appendix A: Generalized ESD test

For a data set which is approximately normally distributed, with mean ($\bar{x}$) and standard deviation (σ) the generalized extreme Studentized deviate (GESD) test (Rosner, 1983) can detect multiple outliers. The test null hypothesis is that there are no outliers in the data set, and the alternate hypothesis is that there are up to r outliers. The test statistic (R_i)

$$R_i = \frac{\max_i |x_i - \bar{x}|}{\sigma}$$

is calculated for the most extreme outlier first (maximum $|x_i - \bar{x}|$), and then that data point (x_i) is removed and the test statistic is recalculated until all potential outliers have been removed.

After calculating the test statistic for each potential outlier ($R_1, R_2, \dots, R_r$), the critical values can be calculated for significance level α :

$$\lambda_i = \frac{(n-i)t_{p,n-i-1}}{\sqrt{(n-i-1+t_{p,n-i-1}^2)(n-i+1)}} \quad i = 1, 2, \dots, r$$

where

$$p = 1 - \frac{\alpha}{2(n-i+1)}$$

and $t_{p,v}$ represents the p th percentile of a t distribution with v degrees of freedom.

The number of outliers is determined by finding the largest i such that $R_i > \lambda_i$.

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