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

4

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19

20

21 **Abstract**

22 The helium isotope composition of air might have changed since the
23 industrial revolution due to the release of ^4He -rich crustal helium
24 during exploitation of fossil fuels. Thereby, variation of the atmospheric
25 helium isotope ratio ($^3\text{He}/^4\text{He}$) has been proposed as a possible new
26 atmospheric tracer of industrial activity. However, the magnitude of
27 such change is debated, with possible values ranging from 0 to about
28 2‰/yr (Sano, 1989; Hoffmann and Nier, 1993; Pierson-Wickmann et
29 al., 2001; Brennwald et al., 2013; Lupton and Evans, 2013). A new
30 analytical facility for high precision (2‰, 2σ) analysis of the $^3\text{He}/^4\text{He}$
31 ratio of air has been developed at CRPG Nancy (France) capable of
32 investigating permil level variations. Previously, Brennwald et al.
33 (2013) analyzed a selection of air samples archived since 1978 at
34 Cape Grim, Tasmania, by the Commonwealth Scientific and Industrial
35 Research Organisation (CSIRO). They reported a mean temporal
36 decrease of the $^3\text{He}/^4\text{He}$ ratio of 0.23-0.30‰/yr. Re-analysis of aliquots
37 of the same samples using the new high-precision instrument showed
38 no significant temporal decrease of the $^3\text{He}/^4\text{He}$ ratio ($0.0095 \pm$
39 0.033% /yr, 2σ) in the time interval 1978-2011. These new data

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

42

43

44 **Introduction**

45 The helium isotopic composition of air may be able to provide a new
46 tracer for studying and quantifying environmental changes resulting
47 from global warming and anthropogenic activity. Due to their light
48 masses, the two isotopes of helium escape to space through thermal
49 and non-thermal processes (Ozima and Podosek, 2002).
50 Consequently, the helium content of air is low (5.24 ppm vol.,
51 Gluckauf, 1946) and the atmospheric He isotope ratio is a transient
52 value determined by variations of the strengths of sources (outgassing
53 of the solid earth, extraterrestrial contributions) and sinks (loss to
54 space) of ^3He and of ^4He over time (Ozima and Podosek, 2002). The
55 He isotope residence time in the atmosphere is of the order of 10^4 - 10^6
56 yr (Torgersen, 1989; Kockarts, 1973), much longer than the
57 atmospheric mixing time of 10 yr. Thus, the $^3\text{He}/^4\text{He}$ ratio of modern air
58 (1.34 - 1.40×10^{-6} , Mamyrin et al., 1969; Clarke et al., 1975; Davidson
59 et al., 1988; Hoffmann and Nier, 1993; Sano et al., 1988) should be
60 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

82 contradictory results, indicating either decreases in the $^3\text{He}/^4\text{He}$ ratio of
83 the order of 0.1-0.3 ‰/yr during the last few decades (Sano et al.,
84 2010; Matsuda et al., 2010), or no detectable change since at least
85 1973 (Lupton and Evans, 2013) or possibly 1956 (Hoffmann and Nier,
86 1993).

87 The study of Brennwald et al. (2013) is particularly relevant,
88 because it presents results of temporal atmospheric helium variations
89 from samples periodically archived in stainless steel containers since
90 1978 (Cape Grim Air Archive (CGAA), Tasmania; Langenfelds et al.,
91 1996). As these samples were collected from a single location,
92 Brennwald et al. (2013) argued that potential problems due to
93 geographical heterogeneities should not apply. Based on a statistical
94 analysis of repeated runs, Brennwald et al. reported a mean decrease
95 of the $^3\text{He}/^4\text{He}$ ratio of 0.23 to 0.30 ‰/yr during this period of time. In
96 contrast, Lupton and Evans (2013) did not observe any significant
97 difference between $^3\text{He}/^4\text{He}$ ratios measured in air samples taken at a
98 single location (La Jolla, California, USA) in 1973 and 2013. Together
99 with other data from different locations and periods of time, they
100 derived a mean rate of decrease of the $^3\text{He}/^4\text{He}$ ratio of
101 $(0.014 \pm 0.045)\text{‰/yr}$ (2σ), which is consistent with zero rate of change
102 over a 40-year period.

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

111

112 **Method**

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

124 Subsamples for $^3\text{He}/^4\text{He}$ analysis were chosen from a selection of
125 ten archive tanks spanning the time period 1978 – 2011: 1978, 1979,
126 1984, 1988, 1993, 1997, 2000, 2004, 2008, 2011 (Table 1). Multiple
127 subsamples were collected from each tank in 1.2-m-long, 3/8"-OD
128 copper tubes, which were sealed by cold-welding with a crimping tool
129 (Brennwald et al., 2013).

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

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

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

165 2013) over the same time period the CGAA sample measurements
166 were made.

167

168 **Results and Discussion**

169 **Helium in the Cape Grim Air Archive**

170 In Table 1, we report measurements from a selection of copper-
171 tube subsamples from the CGAA. Particular effort was made to make
172 multiple measurements from the earliest (1978, 1979) and latest
173 (2008, 2011) subsamples since these would be the most likely to show
174 a detectable difference and would best constrain the trend over the
175 time period.

176 Three of the data points are statistically significant outliers. The
177 $^3\text{He}/^4\text{He}$ from 1988 and 2004 are 10-20‰ lower than all the other data
178 points, while the $^3\text{He}/^4\text{He}$ ratio of the 1984 subsample is about 4‰
179 lower than in the other samples (excluding 1988 and 2004). A
180 generalized extreme Studentized deviate (GESD) test (Appendix A,
181 Rosner, 1983) confirms the 1988 and 2004 data points as outliers with
182 99% confidence whether the test is run using the ratios or the
183 residuals of a best-fit linear time trend. This test assumes the dataset

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

186 The 1984 tank at CSIRO is suspected of having a small leak as was
187 noted in Brennwald et al. (2013). The nitrogen isotopes in this
188 particular storage tank were detectably fractionated and additional
189 testing showed a change in the relative concentrations of H₂, CH₄,
190 CO₂, and N₂O over time (Brennwald et al., 2013). These indicate a
191 small leak in this storage tank which would lead to a decrease in the
192 ³He/⁴He over time as slightly more ³He effused out of the tank relative
193 to ⁴He, consistent with our data showing a lower ³He/⁴He ratio relative
194 to the other samples. We can correct for this effect using observed
195 changes in the concentrations of H₂, CH₄, CO₂, and N₂O and
196 Graham's Law to calculate the expected fractionation of the helium
197 isotopes (as in Brennwald et al., 2013). The correction increases the
198 1984 ³He/⁴He by about 3.5‰, bringing it to well within the scatter of
199 the rest of the data excluding 1988 and 2004 (Table 1). Neither the
200 1988 nor 2004 tanks at CSIRO show any evidence of leakage. Thus, it
201 seems likely that these samples were fractionated at some point after
202 subsampling, e.g., during storage or aliquoting of the subsamples. In
203 the following discussion, we will consider both the uncorrected and
204 effusion-corrected 1984 data but will exclude the 1988 and 2004 data.

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

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

210

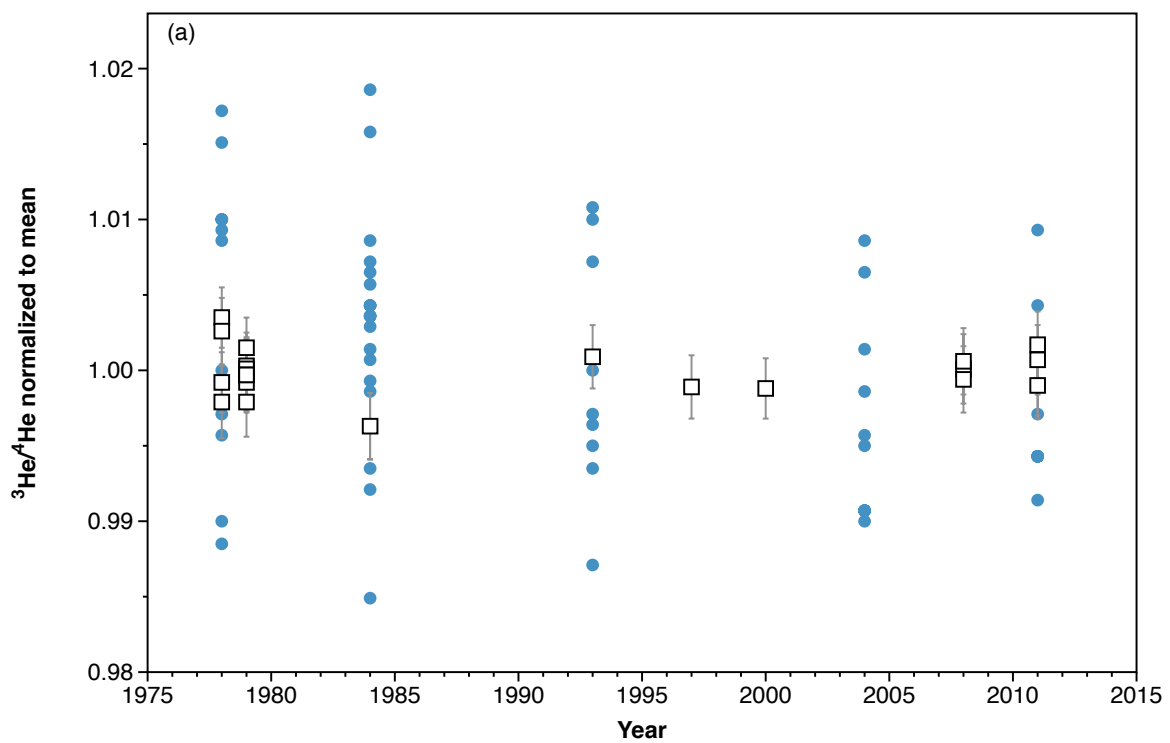
211 An error-weighted least-squares fit (e.g. Baird, 1995) of the
 212 $^3\text{He}/^4\text{He}$ with the uncorrected 1984 ratio (excluding 1988 and 2004)
 213 results in a trend line with a slope that is essentially zero: $(0.000 \pm$
 214 $0.033)\%/\text{yr}$ (2σ , Fig 1b). If the potential effusion effect on the $^3\text{He}/^4\text{He}$
 215 value obtained from the 1984 tank is considered, the slope

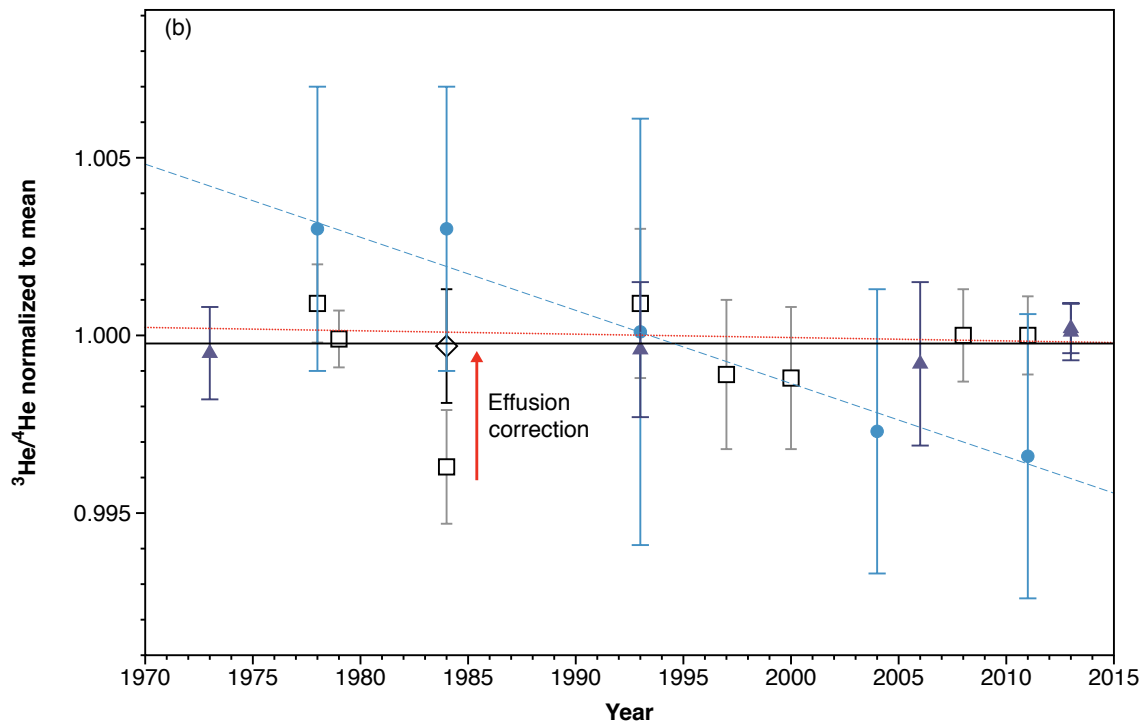
216 corresponds to a $^3\text{He}/^4\text{He}$ decrease of $(0.0095 \pm 0.033)\%/\text{yr}$ (2σ ,
217 Fig 1b). The $^3\text{He}/^4\text{He}$ time series is therefore consistent with a constant
218 $^3\text{He}/^4\text{He}$ ratio and is constrained to a rate of decrease of less than
219 $0.033\%/\text{yr}$ (2σ , assuming no effusion) or $0.042\%/\text{yr}$ (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

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

264 These predicted He concentrations come primarily from the U.S.
265 Bureau of Land Management's (previously Bureau of Mines) survey of
266 natural gas compositions (see e.g BLM, 2008). A straight average of
267 the helium compositions contained in this database yield an average
268 helium content of around 0.25 – 0.3%. However, Lupton and Evans
269 (2013) noted that this data shows an inverse correlation between
270 helium content and reported production rate (open flow) of the well,
271 indicating that there may be an inverse relationship between helium
272 content and field size. Weighting the helium data by open flow brings
273 the average down to around 0.15%. Additionally, this database may
274 over-represent higher helium wells since it includes primarily data from
275 U.S. wells (~16,700 U.S. records vs 133 non-U.S.) which may have a
276 higher helium content than the rest of the world (non-U.S. average
277 helium content ~ 0.06%). And this database may even over-sample
278 higher helium wells within the U.S. as well since helium is an important

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

281 If we look directly at helium production, Mohr and Ward (2014)
282 estimate that $\sim 2.0 \times 10^{11}$ moles were produced world wide between
283 1921 and 2012. Assuming most of this helium made its way into the
284 atmosphere within a few years, it would lead to a decrease in the
285 atmospheric $^3\text{He}/^4\text{He}$ of about 0.0025‰/yr (or about 0.225‰ over the
286 91-year span). Narrowing the focus to just the period 1978-2011, we
287 have about 1.5×10^{11} moles produced world wide (U.S. Geological
288 Survey, 2014), leading to a decrease in the atmospheric $^3\text{He}/^4\text{He}$ of
289 about 0.005‰/yr (or about 0.15‰ over the 33-year span). If we further
290 assume that helium is being extracted from most of the high-helium
291 natural gas wells, then the average helium content for the remaining
292 wells would be much lower. After accounting for helium production and
293 using an average natural gas production over the last three decades of
294 $\sim 1 \times 10^{14}$ mol/yr (IEA, 2014), then we find the average helium content
295 of natural gas consistent with our data is at most 0.034% (2σ
296 maximum). This is roughly 3 - 7× lower than the commonly quoted
297 values of 0.1-0.25%.

298

299 **Conclusion**

300 We have re-analyzed the He isotope composition of a series of air
301 aliquots sampled at Cape Grim, Tasmania, and stored in stainless
302 steel taken by CSIRO. We do not observe any significant change in
303 the $^3\text{He}/^4\text{He}$ ratio over this time period and find the maximum rate of
304 decrease to be $0.033 - 0.042\text{‰/yr}$ (2σ); two outliers (1988 and 2004)
305 have been excluded from the compilation. We do not reproduce the
306 result of Brennwald et al. (2013), who, based on the analysis of air
307 aliquots from the same series reported a decrease of $(0.23 - 0.30 \pm$
308 $0.16)\text{‰/yr}$ of the $^3\text{He}/^4\text{He}$ ratio between 1978 and 2011. Our results
309 are consistent with previous reports that the He isotope composition of
310 air has not changed by more than 0.059‰/yr (2σ) between 1973 and
311 2013 (Lupton and Evans, 2013), and with the results of Hoffmann and
312 Nier (1993) who concluded there was no significant change in the
313 $^3\text{He}/^4\text{He}$ ratio based on measurements done on air collected between
314 1956 and 1988. Our data suggests that the commonly reported mean
315 concentration of helium in natural gas is significantly over-estimated
316 (at least $3\times$) and is likely no more than 0.034% .

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

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

325

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333 Paul Steele for helpful discussions relating to this work. Thanks also to helpful
334 comments from two anonymous reviewers, and to Editor Derek Vance.

335

336 **Appendix A: Generalized ESD test**

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

$$342 \quad R_i = \frac{\max_i |x_i - \bar{x}|}{\sigma}$$

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

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

$$348 \quad \lambda_i = \frac{(n-i)t_{p,n-i-1}}{\sqrt{(n-i-1+t_{p,n-i-1}^2)(n-i+1)}} \quad i = 1, 2, \dots, r$$

349 where

$$350 \quad p = 1 - \frac{\alpha}{2(n-i+1)}$$

351

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

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

354

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