

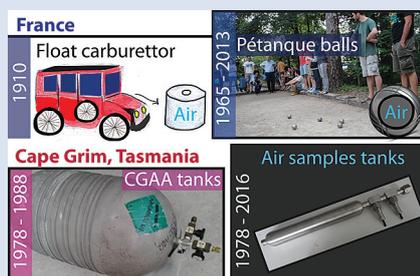
# Atmospheric helium isotopic ratio from 1910 to 2016 recorded in stainless steel containers

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doi: 10.7185/geochemlet.1804

## Abstract



The atmospheric helium isotope composition ( $R_A = {}^3\text{He}/{}^4\text{He}_{\text{air}} = 1.39 \times 10^{-6}$ ) could have varied over recent times due to anthropogenic activities. In order to check this possibility, we conducted high-precision helium isotope measurements of air trapped in various stainless steel containers from France (pétanque balls, a float carburettor; 1910–2016) and Cape Grim, Tasmania (archived air tanks; 1978, 1988). We used a double collector mass spectrometer at the Centre de Recherches Pétrographiques et Géochimiques (CRPG, Nancy, France). We found a similar composition between the French and Cape Grim air samples. The temporal variation estimated from all samples including data previously published is not significant, with a trend of  $+0.002 \pm 0.024 \text{ ‰/yr}$  over 106 years ( $2\sigma$ ). We suspect that the release of radiogenic  ${}^4\text{He}$  by fossil fuel exploitation could have been at least partly offset by the production of  ${}^3\text{He}$  (via the decay of  ${}^3\text{H}$ ) from nuclear tests. This study supports the suitability of atmospheric helium as an inter-laboratory isotope standard.

Received 7 October 2017 | Accepted 29 January 2018 | Published 19 February 2018

## Introduction

Atmospheric helium is a trace gas used as an international standard, whose abundance and isotope composition may be impacted by anthropogenic activities (e.g., Sano *et al.*, 2010). It is therefore of the utmost importance to check if the atmospheric  ${}^3\text{He}/{}^4\text{He}$  ratio ( $R_{\text{AIR}}$ ) has, or has not, been constant over time. According to Oliver *et al.* (1984), the exploitation of natural gases (NG) could have increased the global atmospheric helium content by 1 to 6 ‰ between 1939 and 1981. Because NG are rich in radiogenic  ${}^4\text{He}$  generated in the continental crust, the  $R_{\text{AIR}}$  could have decreased by  $\leq 3 \text{ ‰/yr}$  (Brennwald *et al.*, 2013 and references therein; see also Fig. S-1). In line with this possibility,  ${}^3\text{He}$  excesses ( $\sim 3\text{--}4 \text{ ‰}$  relative to the present  $R_{\text{AIR}}$  value) have been reported for old air trapped in vesicles of blast-furnace metallurgical slags (Pierson-Wickman *et al.*, 2001; Sano *et al.*, 2010) and in ancient porcelains (Matsuda *et al.*, 2010), suggesting that pre-industrial air contained less  ${}^4\text{He}$  than the present-day air. However, these excesses might also be related to: (i) the release of cosmogenic/nucleogenic  ${}^3\text{He}$  from the sample matrix; (ii) isotope fractionation during helium extraction and (iii) the capture of fractionated  $R_{\text{AIR}}$  during manufacturing (Pierson-Wickman *et al.*, 2001).

The occurrence of temporal variations of the  $R_{\text{AIR}}$  value has been questioned in several studies. Lupton and Evans (2013) did not detect significant variations in Pacific marine air from La Jolla, California, USA (trend of  $-0.014 \pm 0.045 \text{ ‰/yr}$  obtained by direct comparison of La Jolla air collected in 1973 and 2013). From the analysis of air sampled in stainless

steel bottles in Tasmania since 1978 (Cape Grim Air Archive, CGAA), Mabry *et al.* (2015) concluded that the  $R_{\text{AIR}}$  value has been stable (trend of  $-0.0095 \pm 0.0330 \text{ ‰/yr}$ ) over the last three decades. These authors argued that the mean helium content of globally produced NG has been overestimated by  $\sim 3$  times in early studies, so that  ${}^4\text{He}$  released by NG may not have impacted the  $R_{\text{AIR}}$  value within the precision of measurements.

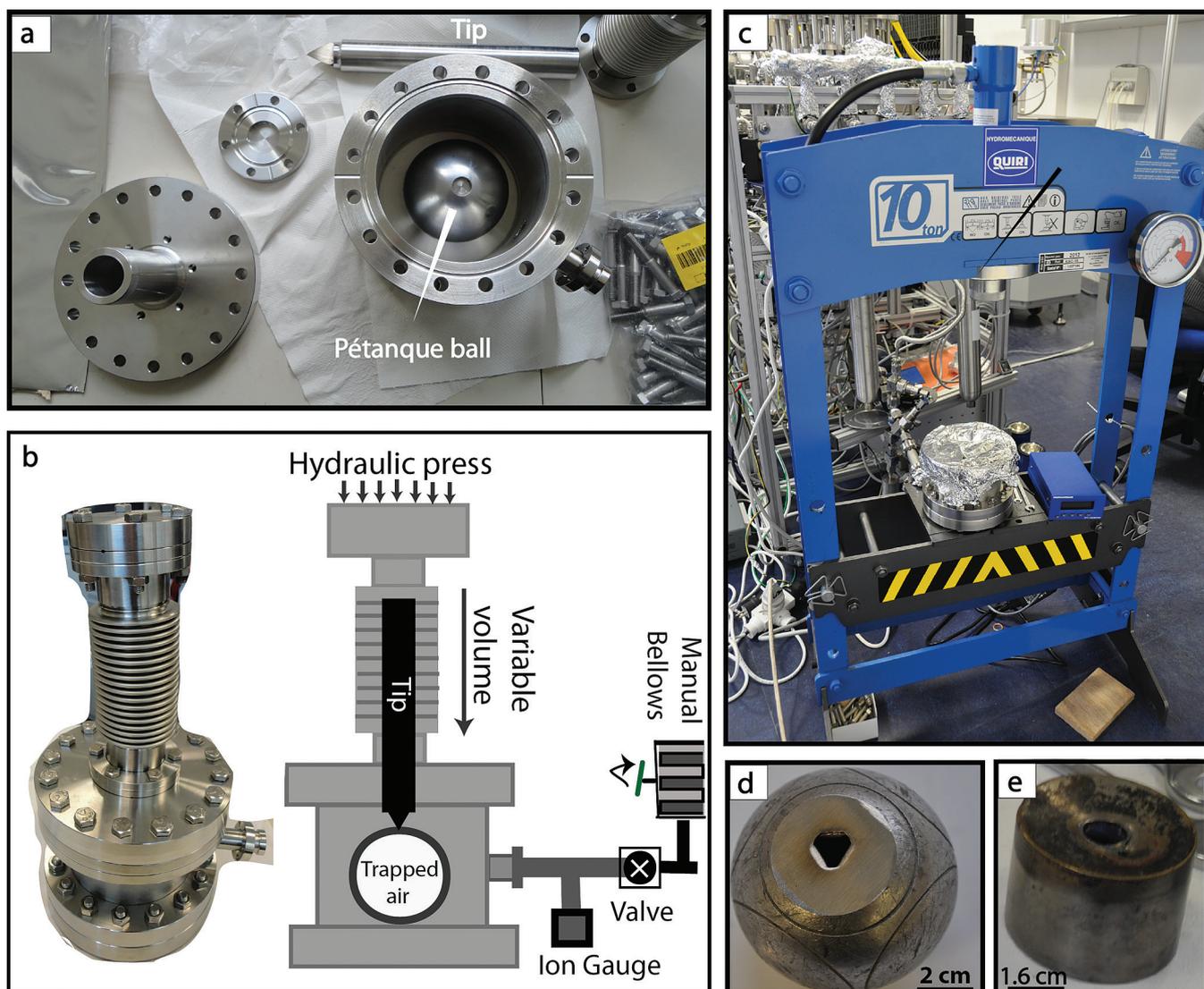
Here, we aim to constrain temporal variation of  $R_{\text{AIR}}$  that could be related to the beginning of the commercial helium production in 1921 (Mohr and Ward, 2014). To do so, we used large amounts of air trapped in stainless steel materials insuring good preservation of helium over time since 1910. The air volume trapped in our selected samples ( $\geq 50 \text{ cm}^3$ ), larger than that trapped in vesicles of slags/porcelains, allows repeated measurements and therefore more precision.

## Methods

**Air sample collection.** At the same location in the Brabois Park (Villers-lès-Nancy, France), two air samples, called BB, were collected in 2014 and 2016, in stainless steel tanks previously put under vacuum. The BB 2014 air, used as an external standard, has been trapped in a 2.3 L tank. The BB 2016 air was collected in a 500  $\text{cm}^3$  tank (Swagelok® 304L-HDF4-500) welded with two stainless steel valves (Swagelok® SS-8BG-TW-VD) placed in series. These valves ensure a safe isolation of the trapped air.

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**Figure 1** (a) Stainless steel chamber. (b) Sectional view of the chamber. (c) Hydraulic press KSC-10. (d) Pétanque ball pierced. (e) Carburettor float.

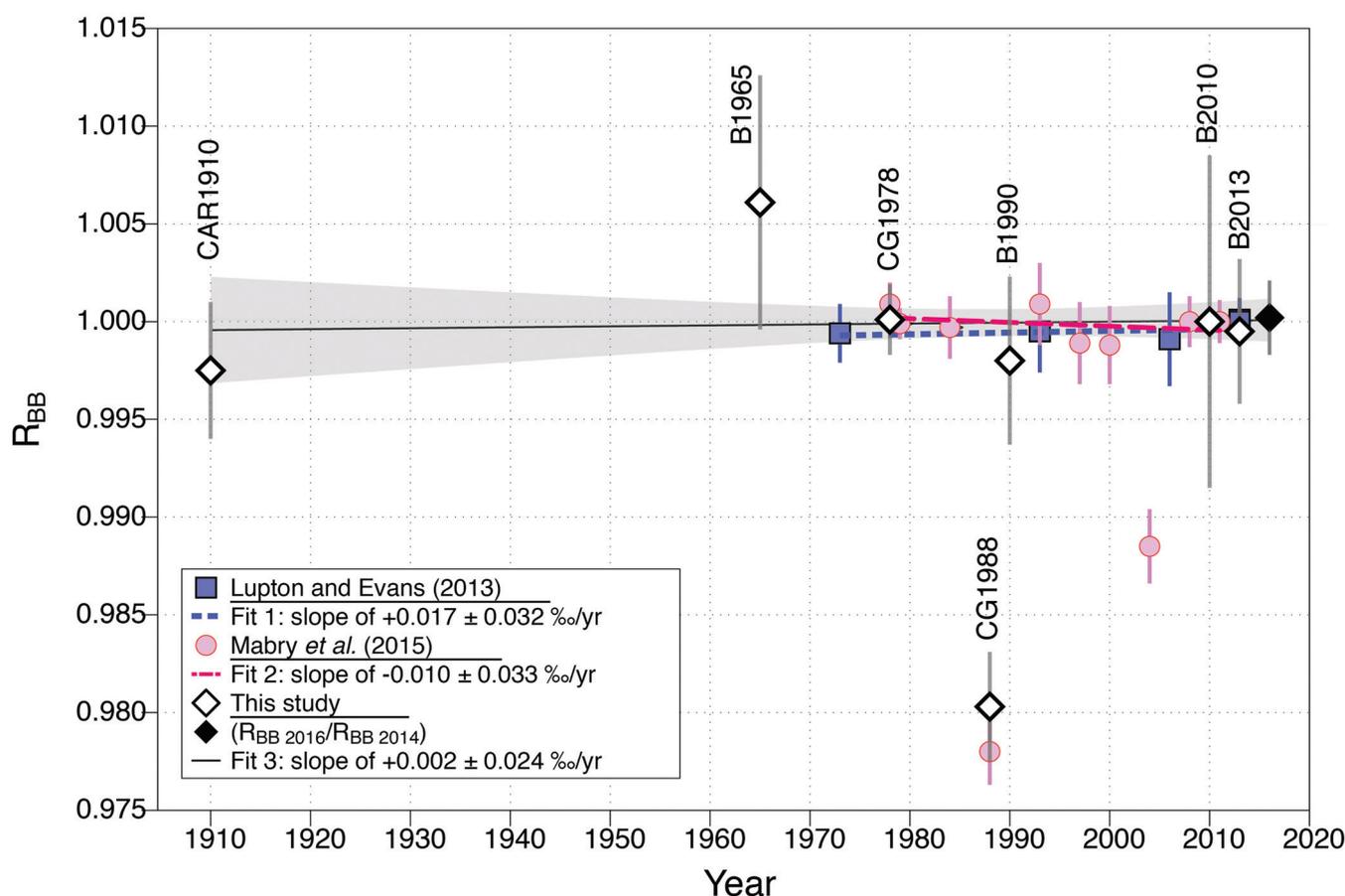
In 500 cm<sup>3</sup> tanks, we also subsampled two air samples from CGAA (1978, 1988). Mabry *et al.* (2015) have previously analysed the He composition of these two samples, through copper tube subsamples (~10–15 cm<sup>3</sup>). We selected these samples because: (i) the 1978 sample was collected during the first storage year of CGAA samples, and (ii) the 1988 sample has previously shown a He isotope composition slightly different from those of other measured CGAA samples.

We obtained a carburettor float of a vintage Renault car (1910) from the Musée de l'Histoire du Fer (Jarville, France) and pétanque balls (manufactured in 1965, 1990, 2010, 2013) from the OBUT<sup>®</sup> company (France). These objects have trapped the air at their manufacturing time. The wall and welding of the carburettor float were inspected for possible microfractures, but none was found. The pétanque balls are made of two half-spheres that trapped ~150 cm<sup>3</sup> of air when welded together. The thickness of the ball walls (~6 mm), observed on X-ray photography, minimises potential fractionation effects linked to microcrack formation. No evidence of leaking was found for the two oldest samples (See Supplementary Information).

***R*<sub>AIR</sub> measurements.** Two stainless steel chambers have been designed to pierce the welded containers (*i.e.* pétanque balls, float reservoir, respectively). They are both composed of a cylindrical volume in which each container is placed, a variable

bellows in which a sharp metal tip is positioned, a Pirani gauge to monitor the pressure, and a manual valve to isolate the chamber (Fig. 1). Their cylindrical volumes and tips were designed to fit the respective sizes of the welded containers. The balls were first abraded to obtain a thin flat surface, easier to pierce with the tip. Each container was placed in its respective chamber, which was closed and pre-evacuated down to ~10<sup>-7</sup> mbar using a turbomolecular pump. After isolation from the pumping system, the tip under the bellows was pressed to the container's wall in order to pierce it using an external hydraulic press (KSC-10 model, Quiri Hydromécanique). The trapped air released in the chamber was left equilibrating to obtain a stable pressure. The connection between the closed chamber and the purification line were baked and degassed for a few hours before each analysis.

For each complete analysis (lasting 9 hours), about 15–20 cm<sup>3</sup> of an air sample (*i.e.* pétanque ball, float reservoir, BB, CGAA) was subsampled and purified with a combination of active charcoal traps held at liquid nitrogen temperature and getters. For the welded containers, the air was transferred into the purification line using a tube and an adjustable bellows connecting the chamber to the line (Fig. 1c). Following the purification, we used a sample-standard bracketing method, which consisted of measuring multiple aliquots of an air



**Figure 2** Error-weighted mean ( $\bar{x}$ ) of the He isotope ratios, expressed as  $R_{BB}$  (diamond points; CG = Cape Grim; B = pétanque ball, CAR = carburettor), over time. Mabry *et al.* (2015) data (pink dots) are also normalised to BB air. Lupton and Evans (2013) data (blue squares) are normalised to 2013 La Jolla air (California, USA). The weighted linear regression fits 1, 2 and 3 are obtained using data of Lupton and Evans (2013), Mabry *et al.* (2015) and the combination of our data with those of Mabry *et al.* (2015), respectively. The uncertainty envelope of fit 3 is shown in grey shaded area. Results are reported at 95 % CI (equivalent to  $2\sigma$ ).

sample alternately with an internal He standard. Simultaneous measurements of  $^3\text{He}$  and  $^4\text{He}$  have been achieved with a split flight tube mass spectrometer (Helix SFT, Thermo Fisher Scientific™). More information about the purification procedure and the analysis are available in Mabry *et al.* (2013) and in the Supplementary Information.

For each analysis, we normalised the He isotopic composition of the air sample ( $R$ ) to the average composition of our external standard BB ( $R_{BB2014}$ ) given its long term reproducibility ( $R_{BB2014} = 1.0300 \pm 0.0014$  at 95 % CI; number of complete analysis =  $N = 26$ ). The internal standard is fractionated relative to BB air since the beginning of its preparation (Mabry *et al.*, 2013). In the following discussion, all data and related estimations are given at the 95 % confidence interval (CI) level.

## Result and Discussion

**$R_{AIR}$  from France (BB tanks, pétanque balls, carburettor float reservoir) and Cape Grim (CGAA).** The normalised isotope ratios ( $R_{BB} = R/R_{BB2014}$ ) of each complete analysis done on air trapped in tanks (CGAA, BB), pétanque balls (B) and in the carburettor float reservoir (CAR) are reported in Table S-1. Each  $\bar{x}$  value represents the error-weighted mean of the  $R_{BB}$  ratios obtained for one air sample, with its related uncertainty (Table S-1). Figure 2 presents the results of Mabry *et al.* (2015) on CGAA as  $\bar{x}$  values when more than one  $R_{BB}$  has been measured, our  $\bar{x}$  values and the results of Lupton and Evans (2013) on Pacific marine air.

**1. The CGAA (1978, 1988).** The  $\bar{x}$  value of the CGAA samples (CG1978, CG1988) are consistent with those previously reported ( $\bar{x}_{1978}$ :  $a = 1.0000 \pm 0.0018$ ,  $b = 1.0009 \pm 0.0011$ ;  $\bar{x}_{1988}$ :  $a = 0.9802 \pm 0.0028$ ,  $b = 0.9780 \pm 0.0017$ ; [a] this study, [b] Mabry *et al.*, 2015). This confirms that (i) the CG1988 sample presents a substantially lower He isotope ratio, and that (ii) both the copper tubes and stainless steel reservoirs well preserved the initial He signature. For the anomalous CG1988 air, trace species ( $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{N}_2\text{O}$ ) measured in its parent tank through time do not show variation since its collection in 1988. However, its composition is anomalous with respect to other records from Cape Grim, including another CGAA sample collected on the same day (Langenfelds *et al.*, 1996). Its relative depletion in  $\text{CO}_2$  (1 ppm, ~ 2.8 ‰),  $\text{CH}_4$  (36 ppb, ~ 21 ‰) and  $\text{N}_2\text{O}$  (2 ppb, ~ 6.5 ‰) suggests a sampling artefact, the nature of which has not been established.

**2. Air sampled in France (1910, 1965, 1990, 2010, 2013, 2016).** The He isotopic composition of BB 2014 air is consistent with that of 2016 ( $R_{BB2016}/R_{BB2014} = 1.0002 \pm 0.0019$ ,  $N = 26$  for each sample). The He composition of BB air is also comparable to that of air trapped in recent balls, which indicates no detectable fractionation effects due to the manufacturing environment. It is also comparable to that of air trapped in the float reservoir CAR1910 ( $\bar{x} = 0.9974 \pm 0.0036$ ) and to all French air samples taking together (weighted mean of  $\bar{x} = 0.9991 \pm 0.0034$ ). The weighted least squares regression fit of the French air  $\bar{x}$  data (B1965, B1990, B2010, B2013, CAR1910) yields a slope of  $+0.019 \pm 0.042$  ‰/yr over the period 1910–2016 ( $+2.0 \pm 4.5$  ‰ over 106 years; Fig. 2). Therefore, we could not detect significant  $R_{AIR}$  variations within the range of uncertainties.



**No evidence of  $R_{AIR}$  variation since 1910.** The air samples of Tasmania and France have indistinguishable helium isotope compositions, whatever the sampling periods (Table S-1; Fig. 2). When including the Mabry *et al.* (2015) data for CGAA (excluding the anomalous results from 1988 and 2004 samples but including the 1984 air sample corrected for effusion; see Mabry *et al.*, 2015), the temporal trend is  $+0.002 \pm 0.024$  ‰/yr between 1910 and 2016 (Fig. 2). This trend is consistent with those of Mabry *et al.* (2015) and Lupton and Evans (2013) within uncertainties.

**NG and nuclear tests impacts on  $R_{AIR}$ .** The global He production from NG has been estimated to be ~954 kilotons over a 79-year span (1935–2014; U.S. Geological Survey, 2014) or ~789 kilotons over a 91-year span (1921–2012; Mohr and Ward, 2014). Assuming that NG helium is purely radiogenic, these amounts would correspond to  $\sim 2.0\text{--}2.4 \times 10^{11}$  moles of  $^4\text{He}$ . If such helium was globally released and homogenised in the atmosphere ( $^4\text{He}$  atmospheric inventory:  $9.3 \times 10^{14}$  mol), the  $R_{AIR}$  could have decreased by  $\sim 0.22$  ‰ (1921–2012; Mohr and Ward, 2014; Mabry *et al.*, 2015) or  $\sim 0.26$  ‰ (1935–2014; U.S. Geological Survey, 2014). Such estimates are rough since the global He production of NG (i) includes an amount of stocked helium not released into the atmosphere; (ii) neglects an unknown amount of He lost into the air by venting/extraction during its production (e.g., Mohr and Ward, 2014) (iii) neglects the poorly defined average He composition (some are rich in  $^3\text{He}$ ; e.g., Pinti and Marty, 2000).

Another potential anthropogenic source of He isotopes is the production of  $^3\text{H}$  by nuclear tests and industry (Lupton and Evans, 2004), as  $^3\text{H}$  decays to  $^3\text{He}$  with a half-life of  $12.32 \pm 0.02$  yr (Lucas and Unterweger, 2000).  $^4\text{He}$  from NG exploitation might have been partly counter-balanced by that of  $^3\text{He}$  produced by nuclear tests. Over the period 1945–1963, the natural tritium background of  $\sim 3.6$  kg has been upset by the input of  $\sim 560$  kg of tritium from weapon tests in the atmosphere (Guétat *et al.*, 2008). By 2008, only 40 kg of anthropogenic  $^3\text{H}$  remained in the environment, indicating that  $\sim 520$  kg of  $^3\text{H}$  has decayed in  $\sim 1.7 \times 10^5$  mol of  $^3\text{He}$ . Over the period 1945–2008, the  $R_{AIR}$  might have increased by  $\sim 0.13$  ‰ assuming efficient mixing of  $^3\text{He}$  in the atmosphere ( $^3\text{He}$  atmospheric inventory:  $1.29 \times 10^9$  mol). This estimate neglects the amount of  $^3\text{H}$  produced by the nuclear industry ( $\sim 0.06$  kg yr $^{-1}$ ; Belot *et al.*, 1996).

## Conclusion

Cape Grim (Tasmania, Australia) and French air samples show a similar He isotope composition. We found no evidence of  $R_{AIR}$  variation in France, between 1910 and 2016 (trend of  $0.019 \pm 0.042$  ‰/yr;  $2\sigma$ ). From the combination of previous CGAA results reported by Mabry *et al.* (2015) with the results of this study, we determine a trend of  $0.002 \pm 0.024$  ‰/yr over the same period of time ( $0.21 \pm 2.54$  ‰ over 106 years). This trend is coherent with the potential  $R_{AIR}$  variations from  $^4\text{He}$  produced by NG and  $^3\text{He}$  derived from nuclear tests, which could have partly balanced each other out. The global helium production from NG could have lowered  $R_{AIR}$  by  $\sim 0.22$  ‰ over 91 years (Mabry *et al.*, 2015), while the release of tritiogenic  $^3\text{He}$  by nuclear tests (1940s–1980s) could have increased this ratio by  $\sim 0.13$  ‰. Exploring the recent cycle of helium isotopes in air will require improved analytical precision by at least one order of magnitude.

## Acknowledgements

This work was supported by the European Research Council (grant No. 267255) and the Deep Carbon Observatory (DCO). Christian France-Lanord and the Musée de l'Histoire du Fer (Jarville, France) are thanked for providing the Renault 1910 float reservoir. The OBUT company and its technical director M. André Dupuy are also gratefully thanked for providing the pétanque balls. We are grateful to the Cape Grim and CSIRO staff, supported by the Australian Bureau of Meteorology, who over many years have been involved in the collection and management of the CGAA. This work is dedicated to our colleague and friend Pete Burnard.

Editor: Bruce Watson

## Additional Information

**Supplementary Information** accompanies this letter at <http://www.geochemicalperspectivesletters.org/article1804>.



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**Cite this letter as:** Boucher, C., Marty, B., Zimmermann, L., Langenfelds, R. (2018) Atmospheric helium isotopic ratio from 1910 to 2016 recorded in stainless steel containers. *Geochem. Persp. Let.* 6, 23–27.

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## ■ Atmospheric helium isotopic ratio from 1910 to 2016 recorded in stainless steel containers

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### ■ Supplementary Information

The Supplementary Information includes:

- Historical Data
- Global Helium Production Database
- He Isotopic Analyses and Results
- Sample Quality
- Table S-1
- Figures S-1 to S-3
- Supplementary Information References

The pétanque game consists of launching metal balls as close as possible to a small wooden ball (the “cochonnet”).

#### ***Historical Data***

Figure S-1 presents an overview of the potential  $R_{AIR}$  variations estimated over distinct periods of time by several authors.

#### ***Global Helium Production Database***

In this study, we have estimated the potential amount of He released in the air from the global He production database of the U.S. Geological Survey (2014). Figure S-2 presents the apparent consumption of He in the U.S. as well as the U.S. and worldwide He production from 1935 to 2015, provided by this database. During the space race and the nuclear weapons tests period, He applications begin to be attractive enough to increase the helium production and its storage in the United States Federal Reserve. It should be noted that the crustal  $^3\text{He}/^4\text{He}$  ratio is about  $0.02 \times R_{AIR}$  (Aldrich and Nier, 1948; Mamyrin and Tolstikhin, 1984).

## He Isotopic Analyses and Results

The He isotopic ratio of each purified air sample aliquot is normalised with those averaging for the internal standard measured before and after this aliquot (Mabry *et al.*, 2013):

$$R_{a,n} = \frac{({}^3\text{He}/{}^4\text{He})_{\text{sample aliquot}}}{[({}^3\text{He}/{}^4\text{He})_{\text{standard before}} + ({}^3\text{He}/{}^4\text{He})_{\text{standard after}}]/2} \quad \text{Eq. S-1}$$

The average of the normalised He isotopic ratios was computed as  $R = \sum_1^n R_{a,n} / n$ , where  $n$  is the number of measured aliquots for the sample. The related error is calculated at the 95 % confidence interval (95 % CI) according to the Student distribution ( $t_{\alpha/2, N-1} \times s/\sqrt{n}$ , where  $s$  = standard deviation of the normalised He isotopic ratios). We assumed that data follows a student's t-distribution linked to the number of aliquots analysed by multi-aliquot analysis, which is lower than 30. Table S-1 presents the normalised ratio  $R_{BB}$ , equivalent to  $R/R_{BB2014}$ .

The uncertainties obtained in this study are slightly higher than those of the Mabry *et al.*'s (2015) study conducted in the same laboratory (CRPG). There are several reasons for this. One of our two cryogenic pumps, directly linked to the mass spectrometer, failed. Therefore, in contrast to Mabry *et al.* (2015), we used only one cryogenic pump linked to the purification line. This change resulted in a slight decrease in the stability of the He isotopic measurements. Furthermore, the He content in one pipette of our internal standard has decreased as a result of its consumption. In order to maintain a high signal to noise ratio, we decided to analyse a smaller number of the sample's aliquots during the sample-standard bracketing analysis (about 5 instead of 10). In this study and in the one of Mabry *et al.* (2015), the uncertainties are related partly to the number of individual measurements carried out during a sample-standard bracketing analysis (also called a multi-aliquot analysis or referred to here as a complete analysis). Our results therefore appear relatively less precise than those reported by Mabry *et al.* (2015).

## Sample Quality

We do not think that helium trapped in containers might have diffused and exchanged with the exterior air for three main reasons. First, the material of our air containers (stainless steel) is thought to be one of the best materials in which helium can be collected and stored for long periods of time. Indeed, diffusion of noble gases in stainless steel is negligible at room temperature (Zhang *et al.*, 2000; Mamyrin and Tolstikhin, 2013). Secondly, despite He being stored in completely different containers during a similar period of time (*e.g.*, the CGAA and the pétanque balls), their measured  $R_{AIR}$  values are comparable. This is consistent with trapping of a common He component not affected by secondary process. Thirdly, we measured the blanks of the experimental chambers with and without our samples (*i.e.* pétanque ball; carburettor) and found similar blank levels after 10–20 minutes in static mode, suggesting negligible leakage of helium from the containers. We also measured the  ${}^4\text{He}/{}^{20}\text{Ne}$  ratios of some of the ancient air samples (*i.e.* B1965, CAR1910), using a small amount of subsampled purified air. The  ${}^4\text{He}/{}^{20}\text{Ne}$  ratios of these air samples are consistent within the error with those of BB ( ${}^4\text{He}/{}^{20}\text{Ne}_{B1965}/{}^4\text{He}/{}^{20}\text{Ne}_{BB2014} = 1.76 \pm 0.89$ ;  ${}^4\text{He}/{}^{20}\text{Ne}_{CAR}/{}^4\text{He}/{}^{20}\text{Ne}_{BB2014} = 1.09 \pm 0.18$ ; 95 % CI), thus suggesting no loss or gain of helium since air entrapment, but admittedly with a low precision.

The pétanque balls and the carburettor float were carefully scrutinised for possible leaks before analysis. In order to check the tightness of the B1965, we used a Nanotom Phoenix X tomograph (Fig. S-3). We were not able to detect any porosity with the resolution of the analyser. Given the thickness of the pétanque balls walls (6 mm), we assume that helium leakage is negligible. In the thin welded zone, we did not find any evidence of manufacturing defaults (Fig. S-3). However, in order to estimate potential diffusion from the welded object (*i.e.* pétanque balls), further studies could (i) load the experimental chamber with He-free gas and/or (ii) increase the time of the static mode for the blank measurement. Furthermore, it is possible that contamination of atmospheric helium by isotopically fractionated He could have happened during manufacturing. In order to ensure that air trapped during manufacturing is representative of ambient air at the time of manufacturing, further works could measure the  ${}^4\text{He}/{}^{20}\text{Ne}$  ratio of the trapped air with a high precision.



**Supplementary Table****Table S-1**  $R_{BB}$  ratios ( $R/R_{BB2014}$ ) of each multi-aliquot analysis (Cape Grim tanks = CG; Pétañque balls = B; Carbuirettor = CAR). For each sample, the weighted means of the  $R_{BB}$  ratios ( $\bar{x}$ ) are reported with their uncertainties ( $\sigma_{R_{BB}}$  at 95 % CI, equivalent to  $2\sigma$ ).

Air samples	Sampling Date	$R_{BB}$	$\sigma_{R_{BB}}$ , 95 % CI
CG1978 (UAN 780002)	1978	0.9974	0.0045
		0.9986	0.0041
		1.0021	0.0039
		0.9953	0.0066
		1.0000	0.0078
		1.0023	0.0037
		1.0023	0.0185
$\bar{x}$		<b>1.0000</b>	<b>0.0018</b>
CG1988 (UAN 880003)	1988	0.9778	0.0058
		0.9828	0.0041
		0.9769	0.0077
		0.9777	0.0085
$\bar{x}$		<b>0.9802</b>	<b>0.0028</b>
B1965	1965	1.0069	0.0213
		1.0068	0.0094
		0.9949	0.0090
		1.0084	0.0052
		1.0078	0.0072
$\bar{x}$		<b>1.0060</b>	<b>0.0065</b>
B1990	1990	0.9932	0.0063
		0.9975	0.0054
		0.9982	0.0064
		1.0061	0.0080
		0.9936	0.0076
		0.9999	0.0055
$\bar{x}$		<b>0.9979</b>	<b>0.0043</b>

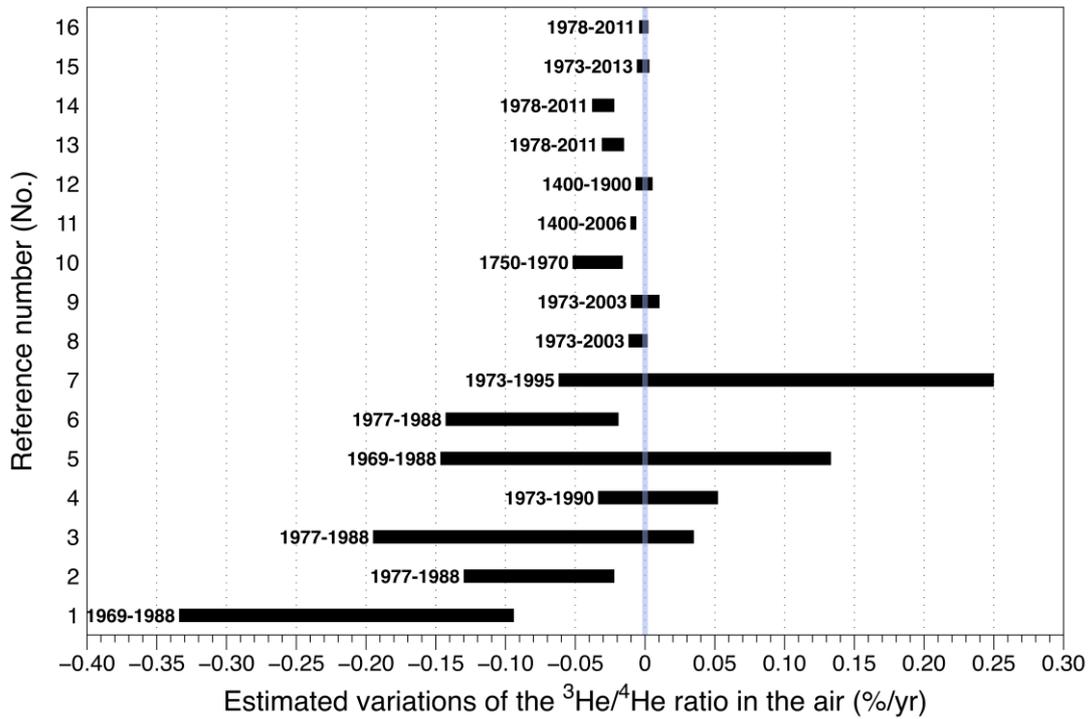


Table S-1 Cont.

Air samples	Sampling Date	$R_{BB}$	$\sigma_{R_{BB}}$ , 95 % CI
B2010	2010	0.9977	0.0115
		1.0028	0.0133
		<b>0.9999</b>	<b>0.0085</b>
$\bar{x}$			
B2013	2013	0.9995	0.0041
		0.9992	0.0102
		<b>0.9994</b>	<b>0.0038</b>
$\bar{x}$			
CAR1910	1910	0.9945	0.0148
		0.9948	0.0127
		0.9978	0.0039
$\bar{x}$		<b>0.9974</b>	<b>0.0036</b>

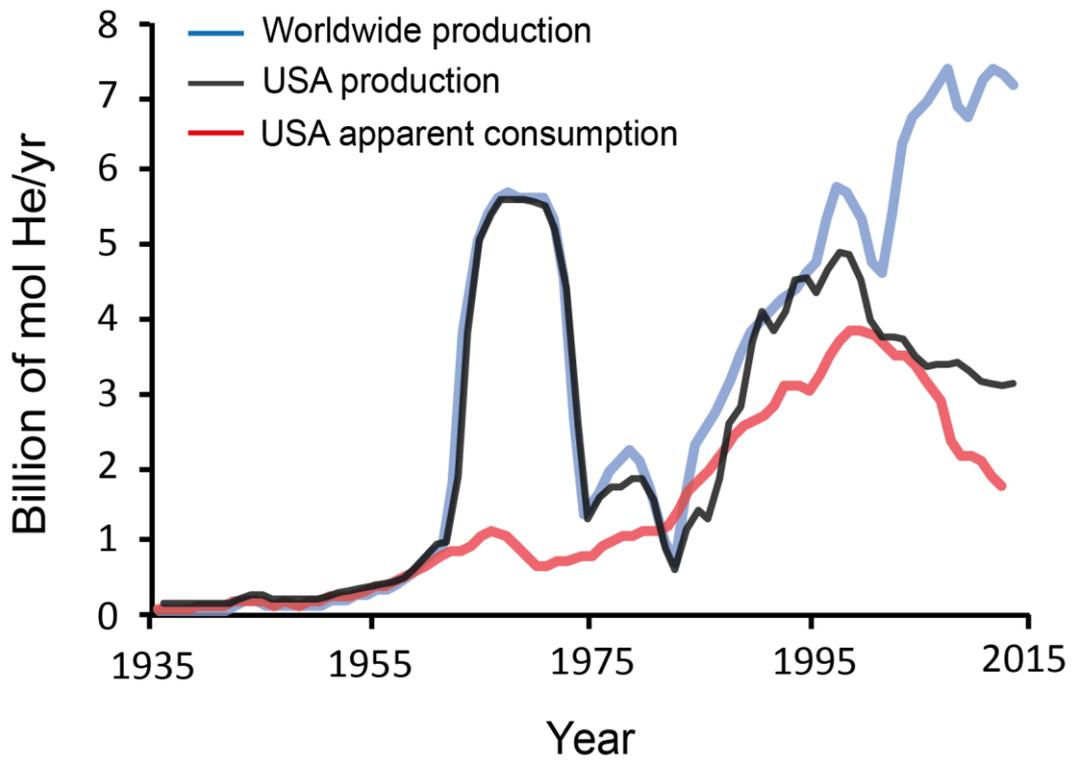


Supplementary Figures

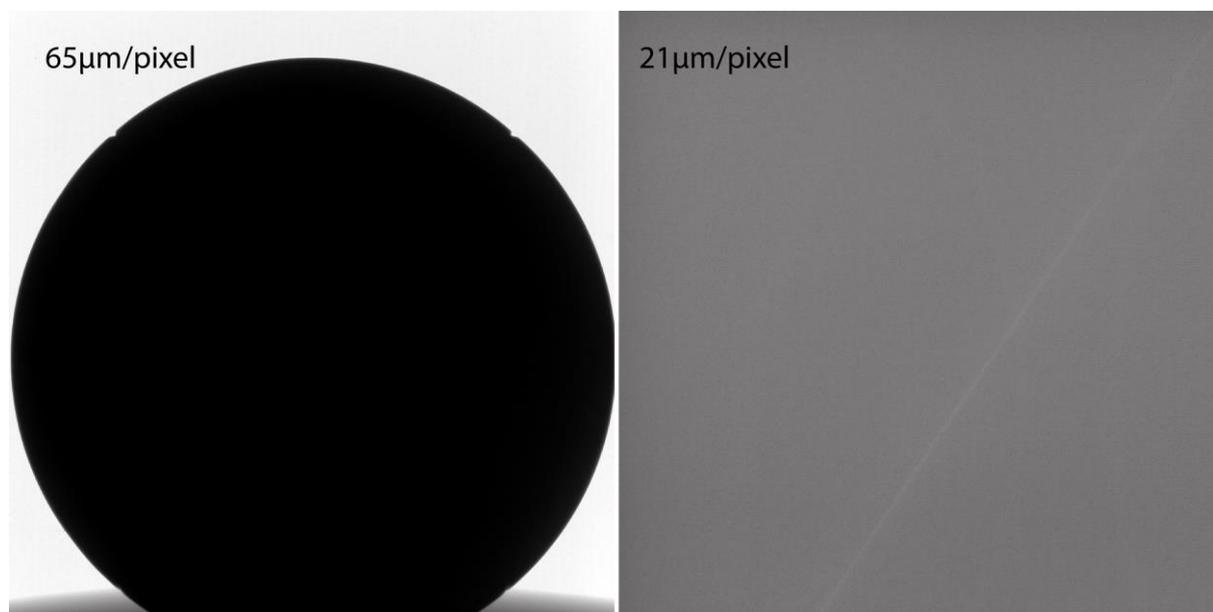


**Figure S-1** Overview of the proposed variations of the  $R_{AIR}$  from several studies. Reference number: (1) Sano *et al.* (1988); (2) Sano *et al.* (1989); (3-5) Lupton and Graham (1991); (6) Sano *et al.* (1991); (7) Sano (1998); (8-9) Lupton and Evans (2004); (10) Matsuda *et al.* (2010); (11-12) Sano *et al.* (2010); (13-14) Brennwald *et al.* (2013); (15) Lupton and Evans (2013); (16) Mabry *et al.* (2015).





**Figure S-2** Helium production and consumption by year reported in the world and in the United States from recent USGS data (U.S. Geological Survey, 2014).



**Figure S-3** Image obtained by a Tomograph X nanotom Phoenix of the B1965. The resolution is not enough to observe features at 65  $\mu\text{m}/\text{pixel}$ . However, we observed the thin welded zone with a resolution of 21  $\mu\text{m}/\text{pixel}$ .

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