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

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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 (2σ). 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.

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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_{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_{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_{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_{AIR} during manufacturing (Pierson-Wickman *et al.*, 2001).

The occurrence of temporal variations of the R_{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_{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 ~ 3 times in early studies, so that ${}^4\text{He}$ released by NG may not have impacted the R_{AIR} value within the precision of measurements.

Here, we aim to constrain temporal variation of R_{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 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 cm³ 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 cm³). 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® 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 cm³ 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_{AIR}* 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 ~10⁻⁷ 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 cm³ 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 2σ).

sample alternately with an internal He standard. Simultaneous measurements of ^3He and ^4He have been achieved with a split flight tube mass spectrometer (Helix SFT, Thermo Fisher Scientific^{TM}). 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 (CO_2 , CH_4 , N_2O) 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 CO_2 (1 ppm, $\sim 2.8 \text{ ‰}$), CH_4 (36 ppb, $\sim 21 \text{ ‰}$) and N_2O (2 ppb, $\sim 6.5 \text{ ‰}$) 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 taken 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 $+0.019 \pm 0.042 \text{ ‰/yr}$ over the period 1910–2016 ($+2.0 \pm 4.5 \text{ ‰}$ 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 ^4He . If such helium was globally released and homogenised in the atmosphere (^4He atmospheric inventory: 9.3×10^{14} mol), the R_{AIR} could have decreased by ~0.22 ‰ (1921–2012; Mohr and Ward, 2014; Mabry *et al.*, 2015) or ~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 ^3He ; e.g., Pinti and Marty, 2000).

Another potential anthropogenic source of He isotopes is the production of ^3H by nuclear tests and industry (Lupton and Evans, 2004), as ^3H decays to ^3He with a half-life of 12.32 ± 0.02 yr (Lucas and Unterweger, 2000). ^4He from NG exploitation might have been partly counter-balanced by that of ^3He produced by nuclear tests. Over the period 1945–1963, the natural tritium background of ~3.6 kg has been upset by the input of ~560 kg of tritium from weapon tests in the atmosphere (Guétat *et al.*, 2008). By 2008, only 40 kg of anthropogenic ^3H remained in the environment, indicating that ~520 kg of ^3H has decayed in $\sim 1.7 \times 10^5$ mol of ^3He . Over the period 1945–2008, the R_{AIR} might have increased by ~0.13 ‰ assuming efficient mixing of ^3He in the atmosphere (^3He atmospheric inventory: 1.29×10^9 mol). This estimate neglects the amount of ^3H produced by the nuclear industry (~ 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 ± 0.042 ‰/yr; 2σ). 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 ± 0.024 ‰/yr over the same period of time (0.21 ± 2.54 ‰ over 106 years). This trend is coherent with the potential R_{AIR} variations from ^4He produced by NG and ^3He derived from nuclear tests, which could have partly balanced each other out. The global helium production from NG could have lowered R_{AIR} by ~0.22 ‰ over 91 years (Mabry *et al.*, 2015), while the release of tritiogenic ^3He by nuclear tests (1940s–1980s) could have increased this ratio by ~0.13 ‰. Exploring the recent cycle of helium isotopes in air will require improved analytical precision by at least one order of magnitude.

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Additional Information

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

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