



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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This paper is dedicated to the memory of our friend and colleague, Peter G. Burnard who passed away too early in a tragic accident

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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 (³He/⁴He) 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 et al., 1989; Hoffman 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 ³He/⁴He 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 ³He/⁴He 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 ³He/⁴He 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.

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1. 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 10⁴–10⁶ yr (Torgersen, 1989; Kockarts, 1973), much longer than the atmospheric mixing time of 10 yr. Thus, the ³He/⁴He ratio of modern air (1.34–1.40 × 10^{−6}, Mamyrin et al., 1970; Clarke et al., 1976; Davidson and Emerson, 1990; Hoffman and Nier, 1993; Sano and Wakita, 1988) should be constant on a decadal timescale. However, it has been suggested that this may no longer be the case (Sano et al., 1989; Pierson-Wickmann et al., 2001; Brennwald et al., 2013; Lupton and Evans, 2013).

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

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

Studies on the atmospheric helium variations, summarized in 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 (Hoffman 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 $(0.014 \pm 0.045)\%$ /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).

2. 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 m³ STP 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

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

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 $^3\text{He}/^4\text{He}$ 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.

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