# Concentrations and isotope ratios of helium and other noble gases in the Earth's atmosphere during 1978–2011

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#### Abstract

The evolution of the atmospheric noble gas composition during the past few decades has hardly been studied because, in contrast to many other atmospheric gases, systematic time-series measurements have not been available. Based on theoretical considerations, the atmospheric noble gas isotope composition is assumed to be stable on time scales of up to about 10<sup>6</sup> years, with the potential exception of anthropogenic changes predicted for the He concentration and the <sup>3</sup>He/<sup>4</sup>He ratio. However, experimental assessments of the predicted changes in the atmospheric He isotope composition are controversial. To empirically test these assumptions and predictions, we analysed the noble gas isotope composition in samples of the

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Cape Grim Air Archive, a well-defined archive of marine boundary layer air in the southern hemisphere. The resulting time series of the <sup>20</sup>Ne, <sup>40</sup>Ar, <sup>86</sup>Kr and <sup>136</sup>Xe concentrations and <sup>20</sup>Ne/<sup>22</sup>Ne and <sup>40</sup>Ar/<sup>36</sup>Ar ratios during 1978–2011 demonstrate the stability of the atmospheric Ne, Ar, Kr and Xe composition during this time interval. The He isotope data provide strong evidence for a decrease in the <sup>3</sup>He/<sup>4</sup>He during the same time interval at a mean rate of 0.23–0.30‰ per year. This result is consistent with most model predictions of the rate of decrease in the atmospheric <sup>3</sup>He/<sup>4</sup>He ratio associated with mining and burning of fossil fuels.

Keywords: air, trace gas, natural gas, fossil fuel, Cape Grim Air Archive

#### 1 1. Introduction

The evolution of numerous trace gases in the terrestrial atmosphere (e.g., CO<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub>, N<sub>2</sub>O, CO, O<sub>3</sub>, SO<sub>2</sub>, nitrogen oxides, halocarbons, etc.) has been monitored and studied very comprehensively during the past few decades (Forster et al., 2007). In contrast, no such systematic research has been conducted on the atmospheric noble gases (He, Ne, Ar, Kr and Xe), although they range among the 10 most abundant trace gases in the dry atmosphere.

The atmospheric composition with respect to Ne, Ar, Kr and Xe isotopes in the 8 atmosphere is generally assumed to be stable on a time scale of about 10<sup>6</sup> years, 9 because there are no known sources or sinks that might modify the atmospheric in-10 ventory of these gases on this time scale (Ozima and Podosek, 2002). In contrast, 11 the concentration of He isotopes in the atmosphere is governed by the dynamic 12 balance of their sources and sinks, i.e., the accumulation of terrigenic He by out-13 gassing of the solid earth, the contribution of extraterrestrial He, and the He loss 14 into space (e.g., Kockarts, 1973; Lupton, 1983; Mamyrin and Tolstikhin, 1984). 15 The mean residence time of He in the atmosphere is approximately  $10^6$  years 16 (Lupton, 1983; Mamyrin and Tolstikhin, 1984). The atmospheric He isotope con-17 centrations resulting from the dynamic balance in the natural geological sources 18 and sinks may be variable on time scales of about 10<sup>5</sup> years or more, but are as-19 sumed to be stable on a time scale of a few millennia (e.g., Lupton, 1983; Oliver 20 et al., 1984; Mamyrin and Tolstikhin, 1984; Pierson-Wickmann et al., 2001). 21

The natural He balance is possibly being disturbed by the release of He isotopes into the atmosphere as a result of anthropogenic activities. In particular, an increase of the He concentration of a few permille during the past few decades has been predicted as a result of the mining and burning of fossil fuels (Oliver et al., 1984). Fossil fuels often contain large amounts of terrigenic He, which is released into the atmosphere during processing and combustion of the fuel. However, detection of the predicted change in the atmospheric He concentration is challenging, because the precisions of currently available methods for determination of He concentrations in air are too low. In addition, chemical transformations of reactive gases (e.g.,  $O_2$ ,  $CO_2$ ,  $H_2O$ , etc.) in an archived air sample might result in a modification of the air matrix and thereby also in the He mole fraction.

An alternative approach to study the evolution of the atmospheric He composi-33 tion is, in analogy to the Suess effect for the carbon isotopic composition of atmo-34 spheric CO<sub>2</sub> (e.g., Tans et al., 1979), to analyse the  ${}^{3}\text{He}/{}^{4}\text{He}$  ratio in archived air. 35 The  ${}^{3}\text{He}/{}^{4}\text{He}$  ratio in fossil fuels ( ${}^{3}\text{He}/{}^{4}\text{He}\approx10^{-8}-10^{-7}$ ) is commonly one to two 36 orders of magnitude lower than the atmospheric ratio  $({}^{3}\text{He}/{}^{4}\text{He}=1.40\times10^{-6})$ . The 37 predicted decrease in the <sup>3</sup>He/<sup>4</sup>He ratio associated with the mining and burning of 38 fossil fuels should be detectable with currently available analytical methods, and 39 is unaffected by chemical transformations of other gas species in the air archive. 40

Indeed, some studies reported experimental evidence for a decreasing  ${}^{3}\text{He}/{}^{4}\text{He}$ 41 ratio in the atmosphere during the past few decades (Sano et al., 1988, 1989; 42 Sano, 1998, see Sec. 2 for an extended literature review). While this decrease in 43 the <sup>3</sup>He/<sup>4</sup>He ratio was interpreted in terms of an anthropogenic input of fossil-fuel 44 derived He into the atmosphere (Sano et al., 1988, 1989; Sano, 1998), other studies 45 questioned the existence of a change in the atmospheric <sup>3</sup>He/<sup>4</sup>He ratio (Lupton 46 and Graham, 1991; Hoffmann and Nier, 1993; Lupton and Evans, 2004). In light 47 of the resulting controversy on the He isotope composition of the atmosphere 48 (Lupton and Graham, 1991; Hoffmann and Nier, 1993; Sano et al., 1991), recent 49 studies attempted to further constrain the change in the <sup>3</sup>He/<sup>4</sup>He ratio on longer 50

time scales by analysing the <sup>3</sup>He/<sup>4</sup>He ratio in air inclusions in ancient porcelain
samples or metallurgical slags (Pierson-Wickmann et al., 2001; Matsuda et al.,
2010; Sano et al., 2010).

However, all experimental He isotope studies conducted so far used hetero-54 geneous sets of air samples taken at different locations. An effect of geographi-55 cal differences in the atmospheric <sup>3</sup>He/<sup>4</sup>He ratio could therefore not be ruled out 56 (Sano et al., 1988, 1989, 2010). In addition, the <sup>3</sup>He/<sup>4</sup>He data obtained from 57 the air inclusions in ancient porcelain and slags may be affected by the release 58 of radiogenic He isotopes from the porcelain or the slags into the air inclusions 59 (Pierson-Wickmann et al., 2001; Matsuda et al., 2010; Sano et al., 2010). Finally, 60 the decrease rates of the <sup>3</sup>He/<sup>4</sup>He ratio determined from the porcelain and slag 61 samples depend strongly on poorly constrained assumptions on the timing and 62 temporal evolution of the  ${}^{3}\text{He}/{}^{4}\text{He}$  ratio in the atmosphere. 63

In summary, the knowledge on the elemental and isotopic noble gas composition of the atmosphere in the past is incomplete and the available He isotope data are inconsistent (see also Sec. 2). While the concentrations of Ne, Ar, Kr and Xe isotopes in the atmosphere are generally assumed to be stable, there are no time series of measured data available that would allow a systematic assessment of this assumption. The He isotope data reported so far resulted in controversial findings on the potential change in the atmospheric He isotope composition in the past.

Robust and precise time series of atmospheric noble gas concentrations and isotope ratios would not only allow constraining the noble gas isotope evolution in the atmosphere per se. New, robust He isotope data would also be useful in applications of the <sup>3</sup>He/<sup>4</sup>He ratio as a proxy for environmental processes. For instance, the atmospheric <sup>3</sup>He/<sup>4</sup>He ratio was discussed as a potential tracer to directly quan-

tify the contribution of the mining and burning of fossil fuels to the accumulation 76 of CH<sub>4</sub>, CO<sub>2</sub> and possibly also other gases in the atmosphere (Sano, 1993; Sano 77 et al., 2010). The atmospheric  ${}^{3}$ He/ ${}^{4}$ He ratio might even allow studying the effect 78 of enhanced groundwater ventilation, which might be linked to global warming 79 (Pierson-Wickmann et al., 2001). Finally, better knowledge about the stability of 80 the atmospheric noble gas composition would be highly useful to noble gas labo-81 ratories, because air is widely used as a standard gas for calibration of most noble 82 gas analysis methods. 83

To determine the noble gas evolution of the atmosphere during the past few 84 decades, we analysed the <sup>20</sup>Ne, <sup>40</sup>Ar, <sup>86</sup>Kr and <sup>136</sup>Xe concentrations and the <sup>3</sup>He/<sup>4</sup>He, 85 <sup>4</sup>He/<sup>20</sup>Ne, <sup>20</sup>Ne/<sup>22</sup>Ne and <sup>40</sup>Ar/<sup>36</sup>Ar ratios in the Cape Grim Air Archive (CGAA) 86 (Langenfelds et al., 1996). The CGAA was established with the specific aim of 87 preserving a record of atmospheric composition, and has been used extensively 88 for the reconstruction of a wide range of atmospheric trace gas histories (e.g., 89 O'Doherty et al., 2009; Mühle et al., 2009, 2010; Vollmer et al., 2011). In con-90 trast to the air archives used in previous He isotope studies, the CGAA tanks were 91 always filled at the same location using consistent experimental methods. To de-92 termine a precise and robust record of the noble gas composition of the Cape 93 Grim air during 1978–2011, we analysed the noble gas isotope composition of 80 94 air aliquots from replicate subsamples of six CGAA tanks. 95

# Potential changes of the atmospheric He composition during the past few decades

The mining and burning of fossil fuels has been postulated as the main source for an increasing He concentration in the atmosphere during the past few decades. The results of previous studies on the possible change in the atmospheric  ${}^{3}\text{He}/{}^{4}\text{He}$ ratio are summarised in Tab. 1.

<sup>102</sup> Modelling studies have predicted an increase in He concentration by 1-6%<sup>103</sup> between 1939 and 1981 (Oliver et al., 1984), and a rate of decrease in <sup>3</sup>He/<sup>4</sup>He <sup>104</sup> ratio during the past few decades of  $(0.14\pm0.07)-(0.85\pm0.3)\%$  per year (E<sub>3</sub>, F <sup>105</sup> and G<sub>1</sub> in Tab. 1; Sano, 1998; Pierson-Wickmann et al., 2001; Lupton and Evans, <sup>106</sup> 2004).

Other potential He sources are the release of <sup>3</sup>He from radioactive decay of 107 synthetic <sup>3</sup>H used in nuclear weapons (Lupton and Evans, 2004), and enhanced 108 ventilation of terrigenic He from groundwaters due to the retreat of ice sheets 109 and thawing of permafrost caused by global warming (Pierson-Wickmann et al., 110 2001). These two processes are not considered further here because their pre-111 dicted rates of change in the atmospheric <sup>3</sup>He/<sup>4</sup>He ratio are at least two orders of 112 magnitude lower than those predicted from the mining and burning of fossil fuels. 113 Trend analyses of <sup>3</sup>He/<sup>4</sup>He ratios measured in archived air or in the deep water 114 of the South Pacific indicated rates of decrease in the atmospheric <sup>3</sup>He/<sup>4</sup>He ratio 115 in the range of  $(0.79\pm0.6)-(2.14\pm0.6)$ % per year (A, B and E<sub>1,2</sub> in Tab. 1; Sano 116 et al., 1988, 1989; Sano, 1998). However, results of other experimental analyses 117 of  ${}^{3}\text{He}/{}^{4}\text{He}$  ratios in air samples were interpreted to be consistent with a constant 118  ${}^{3}\text{He}/{}^{4}\text{He}$  ratio in the atmosphere (C, D<sub>1.2</sub>, G<sub>2.3</sub> in Tab. 1), and indicated the decrease 119 of the atmospheric  ${}^{3}\text{He}/{}^{4}\text{He}$  ratio during 1973–2003 to be less than 0.1% per 120 year on the 95% confidence level (Lupton and Graham, 1991; Lupton and Evans, 121 2004). This constraint is consistent with the decrease rate of the atmospheric 122 <sup>3</sup>He/<sup>4</sup>He ratio predicted by a recent mass-balance model (F in Tab. 1), but not 123 with the higher rates determined from other models ( $E_3$  and  $G_1$ ) or measured data 124

125 (A, B and  $E_{1,2}$ ).

In recent studies (H and  $I_{1,2}$  in Tab. 1), <sup>3</sup>He/<sup>4</sup>He ratios measured in air in-126 clusions in porcelain samples dating back to 1400 AD and in metallurgical slags 127 dating back to 900 AD were used to study the decrease rate of the atmospheric 128 <sup>3</sup>He/<sup>4</sup>He ratio on centennial time scales. However, the quantification of the change 129 in the atmospheric  ${}^{3}\text{He}/{}^{4}\text{He}$  ratio might be affected by the release of radiogenic He 130 isotopes from the porcelain or slag matrices into the air inclusions. Furthermore, 131 the rate of decrease in the  ${}^{3}\text{He}/{}^{4}\text{He}$  ratio calculated from the  ${}^{3}\text{He}/{}^{4}\text{He}$  ratios mea-132 sured in the porcelain samples (H) is based on the arbitrary assumption of a con-133 stant <sup>3</sup>He/<sup>4</sup>He ratio until 1750 AD, followed by a linear increase of the <sup>3</sup>He/<sup>4</sup>He 134 ratio. However, this assumption is inconsistent with the <sup>3</sup>He/<sup>4</sup>He ratios determined 135 in the slag samples  $(I_{1,2})$ , which suggest that the <sup>3</sup>He/<sup>4</sup>He ratio has remained ap-136 proximately constant until about 1900 AD. 137

Up until now, all experimental determinations of the potential change in the 138 atmospheric <sup>3</sup>He/<sup>4</sup>He ratio during the past few decades used samples reflecting the 139 atmospheric <sup>3</sup>He/<sup>4</sup>He ratio at different geographical locations (Tab. 1). However, 140 the atmospheric  ${}^{3}\text{He}/{}^{4}\text{He}$  ratio may be variable on regional or global scales. For 141 instance, a slightly higher <sup>3</sup>He/<sup>4</sup>He ratio was observed in the southern hemisphere 142 than in the northern hemisphere (Sano et al., 2010), where most of the fossil fuels 143 are mined and burned. Such geographical variations can therefore not be ruled 144 out and may therefore present a possible source of error in the experimentally 145 determined decrease rates of the atmospheric <sup>3</sup>He/<sup>4</sup>He ratio during the past few 146 decades (Sano et al., 1988, 1989). 147

#### 148 **3. Methods**

#### 149 3.1. Cape Grim Air Archive (CGAA)

The CGAA is a collection of gas tanks filled with air at the the Cape Grim 150 Baseline Air Pollution Station, northwest Tasmania (Langenfelds et al., 1996). 151 Since 1978, more than 100 gas tanks have been filled with approximately  $1-2 m_{STP}^3$ 152 of pressurised air at intervals of about three months (22.414  $m_{STP}^3 \equiv 10^3$  mol). The 153 tanks are filled under wind conditions where the trajectories of sampled air masses 154 extend back over the 'clean air sector' (190°-280°) of the Southern Ocean. This 155 avoids contributions of mainland air masses that may be influenced by industrial 156 or terrestrial exchange processes. 157

Cape Grim air is archived mostly in 35-L stainless steel tanks (Essex Cryogen-158 ics, Missouri, USA) which are internally electropolished and sealed with bellows-159 type valves. Since construction of the station building in the early 1980s, air has 160 been drawn from the top of a 10 m high tower through a stainless-steel sampling 161 tube (10 cm outer diameter, OD) at a flow rate of approximately  $0.3 \text{ m}_{\text{STP}}^3/\text{min}$ . A 162 previously flushed and evacuated tank is connected via thin tubing (1/4" OD) to 163 a branch connection at the sampling tube. The tank is then cooled to 77 K using 164 liquid nitrogen, and the tank valve is opened to allow a split of the air flow through 165 the sampling tube to expand into the tank. N<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>O and other gases are trapped 166 in the tank by condensation on the cold tank surfaces, which maintains a steady 167 air flow into the tank. The high gas-flow velocity in the thin tubing connecting the 168 tank to the sampling tube prevents back flow of non-condensable gases (e.g., as 169 verified by close agreement of H<sub>2</sub> concentrations measured in CGAA tanks with 170 those observed in CSIRO's parallel flask sampling program at Cape Grim). Fill-171 ing of the archive tank is stopped after approximately 140 min by closing the tank 172

valve. After equilibration to ambient temperature, the tank is inverted such that the valve points downwards, which is then briefly opened to expel the liquid water out of the tank. The oldest (1978) sample was collected before the station building and 10 m tower existed. This air was sampled from the cliff-top using a portable mast, with a gas flow of approximately  $0.02 \text{ m}_{\text{STP}}^3$ /min. The tank was flushed for 30 min and then filled cryogenically using the same procedure as described above for later sampling events.

Assessment of the integrity of the archived air in the CGAA tanks is aided 180 by past analyses of various trace gases and isotopes, such as the concentrations of 181 H<sub>2</sub>, CH<sub>4</sub>, CO<sub>2</sub>, N<sub>2</sub>O and various halogenated compounds, O<sub>2</sub>/N<sub>2</sub> and Ar/N<sub>2</sub> ratios, 182  $^{15}$ N/ $^{14}$ N ratio in N<sub>2</sub> and  $^{18}$ O/ $^{16}$ O ratio in O<sub>2</sub> (Langenfelds et al., 1996; Langenfelds, 183 2002; Langenfelds et al., 2005; O'Doherty et al., 2009; Mühle et al., 2009, 2010; 184 Vollmer et al., 2011). In some cases these data have been validated by compari-185 son to results from parallel, independent sampling programs (Langenfelds et al., 186 1996). Some species have been measured repeatedly over many years providing 187 insight into the stability of the archived air composition (Langenfelds et al., 1996). 188 This information is useful for identifying processes responsible for modification 189 of the archived air in the tanks. 190

The CGAA tanks used for this study were selected to (i) be evenly distributed over the longest possible period (1978–2011) and (ii) have exhibited maximum integrity of trace gas composition with respect to processes that could influence the noble gas composition of the archived air. Because the noble gases are chemically inert, the main aim was to avoid artefacts resulting from mass-dependent fractionation. Previous studies showed that some of the oldest batch of 35-L CGAA tanks used until 1988 had developed microscopic leaks at welded sites on their surfaces,

resulting in small leaks and varying degrees of mass-dependent fractionation of 198 the stored air (Langenfelds, 2002). A direct indicator of such fractionation avail-199 able to us was from CGAA measurements of  $^{15}\text{N}/^{14}\text{N}$  ratios in  $N_2$  and related 200 species made in 2001 (Langenfelds, 2002). Based on these data we selected a 201 subset of CGAA tanks containing air that was expected to be negligibly fraction-202 ated for the purposes of the present study. All but one of the selected CGAA 203 tanks used in this study showed no detectable anomaly in  $^{15}\mathrm{N}/^{14}\mathrm{N}$  ratios in  $\mathrm{N}_2$ 204 with values within  $\pm 0.005\%$  of modern atmospheric air. Only one tank (filled in 205 1984) showed a marginally significant increase of the  $^{15}\text{N}/^{14}\text{N}$  ratio by 0.012%206 in 2001. While CSIRO is not equipped to repeat the <sup>15</sup>N/<sup>14</sup>N analyses at this 207 time, subsequent trace-gas analyses of the air in this tank at CSIRO suggest that 208 between 2001 and 2011 the rate of fractionation has increased. Significant varia-209 tions are evident in the concentrations of  $H_2$  (22<sup>%</sup> decrease during 2001–2011), 210  $CH_4$  (2.1‰ decrease),  $CO_2$  (1.4‰ increase) and  $N_2O$  (2.0‰ increase). The rel-211 ative concentration variations among these species are consistent to within mea-212 surement uncertainty with fractionation due to gas molecules escaping through a 213 narrow orifice whose diameter is small compared to the mean free path length of 214 inter-molecular collisions (effusion). Graham's Law states that the rate of effusion 215 of a given gas species from the tank is inversely proportional to the square root of 216 the molecular mass of this species. We will therefore use Grahams Law to assess 217 possible noble gas fractionation in the 1984 tank. Recent CSIRO analyses of H<sub>2</sub>, 218 CH<sub>4</sub>, CO<sub>2</sub> and N<sub>2</sub>O show no evidence of any significant fractionation in the other 219 five CGAA tanks considered here. 220

#### 221 3.2. CGAA subsampling and noble gas analysis

Subsamples for noble gas analysis were transferred from six CGAA tanks 222 (filled in 1978, 1984, 1993, 2004, 2010 and 2011; Tab. 3) into 1.2 m long copper 223 tubes (3/8" OD) at CSIRO Aspendale (Australia). The CGAA tanks were fitted 224 with internally electropolished, stainless steel regulators (Tescom), separated from 225 the tank valve by a 0.6 m length of 1/16" OD stainless steel tubing. A 1 m length 226 of 1/16" OD stainless steel tubing connected the regulator to the copper tube. A 227 further 1 m length of 1/16" OD stainless steel tubing was attached to the outlet of 228 the copper tube to prevent back diffusion of ambient air into the copper tube during 220 subsampling, and led to a manifold fitted with a pressure gauge, needle valve and 230 flowmeter to control gas flow during sampling. Before gas transfer from the tank 231 into the copper tube, the copper tube was evacuated to remove ambient air using 232 an electric diaphragm pump attached to the manifold. Air flow was then com-233 menced, and maintained at a rate of about  $20 \text{ cm}_{\text{STP}}^3/\text{min}$  with air pressure in the 234 copper tube held steady at 145 kPa for a flushing period of 10–30 min. These flow 235 parameters were selected to minimise the potential for mass-dependent fraction-236 ation, as guided by results of gas transfer tests reported previously (Langenfelds 237 et al., 2005). Finally the copper tube was sealed at both ends using a crimping 238 tool. Multiple replicate subsamples were taken from each CGAA tank. 239

The noble gas isotope compositions in the CGAA subsamples (copper tubes) were analysed in the Noble Gas Laboratory at ETH Zurich (Switzerland). Multiple air aliquots (0.04–0.7 cm<sup>3</sup><sub>STP</sub>) from each subsample were analysed by static mass spectrometry (Beyerle et al., 2000). After transferring an aliquot into the gas purification system, the copper tube was re-sealed, and the air aliquot was separated into a He-Ne fraction and an Ar-Kr-Xe fraction in the purification sys-

tem using a series of cold traps cooled by liquid nitrogen. A first split of the 246 He-Ne fraction was used for combined analysis of <sup>4</sup>He, <sup>20</sup>Ne, and <sup>22</sup>Ne using 247 a custom-built sector-field mass spectrometer equipped with a Baur-Signer ion 248 source (Baur, 1980). After He-Ne analysis, the Ar-Kr-Xe fraction was used for 249 combined analysis of <sup>36</sup>Ar, <sup>40</sup>Ar, <sup>86</sup>Kr, and <sup>136</sup>Xe using the same mass spectrome-250 ter. A second split of the He-Ne fraction was further purified using a cryo trap at 251 70 K and subsequently used for  ${}^{3}\text{He}/{}^{4}\text{He}$  analysis in a Micromass 5400 sector-field 252 mass spectrometer equipped with a Nier-type ion source. The isotope concentra-253 tions and ratios measured in the different gas aliquots from the same subsample 254 were independent of the aliquot size, because the design of the Baur-Signer ion 255 source inherently minimises changes in sensitivity as a function of the gas pressure 256 in the mass spectrometer, and the Nier-type ion source is tuned for gas-pressure 257 independent <sup>3</sup>He/<sup>4</sup>He ratio measurement instead of maximum sensitivity. Cor-258 rection of non-linearities of the mass-spectrometer results obtained from different 259 gas amounts (Tab. 3) was therefore not necessary. Mass spectrometric results were 260 calibrated using aliquots of an air standard collected in Zurich (Switzerland) on 7 261 June 1996 (Tab. 2), which were processed exactly in the same way as the CGAA 262 subsample aliquots. 263

The standard errors for the noble gas concentrations and isotope ratios determined in the individual gas aliquots correspond to the standard deviations of the results of the standard analyses (Beyerle et al., 2000), which are listed in Tab. 2. We found that the total analytical precision is controlled mainly by the preparation and cleaning of the gas aliquot, whereas the uncertainties of the gas analysis in the mass spectrometers are of minor importance on the overall precision. To improve precision and robustness of the results of each CGAA tank, several gas aliquots were analysed from each subsample. To take into account potential effects associated with the gas transfer from the CGAA tanks into the subsample tubes on the overall data precision, air aliquots were taken from different subsample replicates of the same CGAA tank. Data values corresponding to the same CGAA tank were then combined by calculating their means and errors of the means.

#### **4. Results and Discussion**

For each CGAA tank, at least nine air aliquots were analysed. These air aliquots were taken from at least two different subsample replicates, respectively. Only for the 2010 tank, all aliquots were taken from the same subsample. The noble gas results from each subsample aliquot as well as the means and standard errors of the means of each CGAA tank are listed in Tab. 3.

The subsamples from the 2010 tank and some of the subsamples of the 2004 282 tank were filled in a laboratory where He is released into the ambient air from gas 283 chromatographic instruments. An ambient air sample collected in this laboratory 284 showed a He concentration of  $35 \text{ ppm}_{vol}$ , which is about 7 times higher than in 285 uncontaminated air. The concentrations of the other noble gases in the laboratory 286 air agreed with those in uncontaminated air. The <sup>4</sup>He/<sup>20</sup>Ne ratio determined in 287 the subsamples filled in this laboratory was about 1.25% higher than in replicates 288 taken in a room with uncontaminated ambient air. Therefore, if the subsamples 289 are assumed to reflect a binary mixture of air from the CGAA tanks and a small 290 amount of He-contaminated ambient air, contamination with ambient air during 291 gas transfer from the tanks into the copper tubes can be constrained to  $\leq 0.2\%$ 292 for all subsamples. To avoid a bias of the He isotope composition determined in 293 the 2004 and 2010 CGAA tanks, the He data from the subsamples filled in the 294

<sup>295</sup> gas-chromatography laboratory were not used ('NA' values in Tab. 3).

### 296 4.1. Stability of neon, argon, krypton and xenon

Fig. 1 shows the time series of the concentrations of <sup>20</sup>Ne, <sup>40</sup>Ar, <sup>86</sup>Kr and <sup>136</sup>Xe and the isotope ratios <sup>20</sup>Ne/<sup>22</sup>Ne and <sup>40</sup>Ar/<sup>36</sup>Ar in the CGAA. The potential effect of effusion due to an assumed leak in the 1984 tank as calculated from Graham's Law is similar to the analytical precision (Fig. 1, dashed extensions of the error bars). The additional uncertainty associated with the potential gas fractionation by effusion from this tank is therefore only marginal.

The <sup>20</sup>Ne, <sup>40</sup>Ar, <sup>86</sup>Kr, <sup>136</sup>Xe, <sup>20</sup>Ne/<sup>22</sup>Ne and <sup>40</sup>Ar/<sup>36</sup>Ar time series do not show 303 any systematic changes or trends (see also statistical test results in Fig. 1). This 304 finding agrees with the assumption that the Ne, Ar, Kr and Xe composition of the 305 Cape Grim air was stable during the past few decades. Also, the error-weighted 306 means of the isotope concentrations and ratios in the CGAA (M in Fig. 1) agree 307 with the composition of the Zurich air used for calibration of the data (Tab. 2). 308 While these findings were to be expected based on theoretical considerations, they 309 are the first systematic and experimental validation of the temporal and spatial 310 uniformness of the <sup>20</sup>Ne, <sup>22</sup>Ne, <sup>36</sup>Ar, <sup>40</sup>Ar, <sup>86</sup>Kr and <sup>136</sup>Xe composition of the 311 atmosphere during the past few decades. 312

# 313 4.2. Variability of helium isotopes

Fig. 2 shows the time series of the <sup>3</sup>He/<sup>4</sup>He ratio in the CGAA. The potential effusion effect on the <sup>3</sup>He/<sup>4</sup>He ratio in the 1984 tank is similar to the analytical precision. A  $\chi^2$  test of the 'no trend' hypothesis (line A in Fig. 2) yields p = 0.05using the uncorrected data or p = 0.005 using the effusion-corrected data. Without considering alternative hypotheses, the 'no trend' hypothesis can therefore only

be rejected on the  $2\sigma$  level using the effusion-corrected data. However, fitting 319 a straight line to the <sup>3</sup>He/<sup>4</sup>He ratio time series by error-weighted least-squares 320 regression (line B in Fig. 2) results in a slope that corresponds to a mean rate of 321 decrease in the  ${}^{3}\text{He}/{}^{4}\text{He}$  ratio of  $(0.23 \pm 0.08)\%$  per year for the uncorrected data 322 or  $(0.30 \pm 0.08)$ % per year for the effusion-corrected data (1 $\sigma$  errors). These two 323 values agree to within their standard errors, and both values are not consistent 324 with a constant  ${}^{3}\text{He}/{}^{4}\text{He}$  ratio during 1978–2011 on the  $2\sigma$  level. In addition, a 325 statistical comparison of the 'linear trend' and 'no trend' models (F-test using the 326 error-weighted sum of squared residuals; Faraway, 2005) shows clearly that the 327 'no trend' model should be rejected in favour of the 'linear trend' model (p =328 0.0031 for the uncorrected data and p = 0.038 for the effusion-corrected data). 329 Our He isotope results therefore provide strong evidence for a slight decrease in 330 the atmospheric  ${}^{3}\text{He}/{}^{4}\text{He}$  ratio during the past few decades. 33

The rate of decrease in the <sup>3</sup>He/<sup>4</sup>He ratio determined from our noble gas iso-332 tope record is consistent with all previously determined rates within their  $2\sigma$  error 333 limits, except rates A, G<sub>2.3</sub> and I<sub>1.2</sub> (Tab. 1, Fig. 3). Rate A was determined from 334 <sup>3</sup>He/<sup>4</sup>He ratios measured in different samples taken at different locations and anal-335 ysed in different laboratories using different instruments and experimental proto-336 cols. The rates  $G_2$  and  $G_3$  were determined from  ${}^{3}\text{He}/{}^{4}\text{He}$  ratios measured in 5 337  $(G_2)$  or 7  $(G_3)$  air samples, which were taken at different geographical locations. 338 These rates also seemed to depend on the standards used for data calibration. The 339  ${}^{3}\text{He}/{}^{4}\text{He}$  ratio decrease rates A, G<sub>2</sub> and G<sub>3</sub> may therefore be affected by differ-340 ences in the samples, methods and instruments used. The <sup>3</sup>He/<sup>4</sup>He ratio decrease 341 rates  $I_1$  and  $I_2$  were determined from  ${}^{3}\text{He}/{}^{4}\text{He}$  ratios measured in ancient slags. 342 These <sup>3</sup>He/<sup>4</sup>He ratios may be affected by the release of radiogenic He isotopes 343

from the slag matrix into the air inclusions. In addition, these data represent the 344 atmospheric <sup>3</sup>He/<sup>4</sup>He ratio before or during the early stages of the industrial revo-345 lution and are therefore expected to yield a lower rate of decrease in the <sup>3</sup>He/<sup>4</sup>He 346 ratio than the rate reflecting the past few decades, when most of the fossil fuels 347 were mined and burned. In contrast, the rate of decrease in the <sup>3</sup>He/<sup>4</sup>He ratio 348 determined in our study is unaffected by geographical differences of the <sup>3</sup>He/<sup>4</sup>He 349 ratio and is based on robust <sup>3</sup>He/<sup>4</sup>He ratios determined in a reliable air archive 350 covering the time range of 1978–2011. 351

The  ${}^{4}\text{He}/{}^{20}\text{Ne}$  ratios we determined in the CGAA are much more precise than 352 than <sup>4</sup>He/<sup>20</sup>Ne ratios determined in previous air archive studies. Our <sup>4</sup>He/<sup>20</sup>Ne 353 data (Fig. 4) might therefore be useful to further constrain the atmospheric <sup>4</sup>He 354 evolution during the past few decades. For instance, if the decrease in the <sup>3</sup>He/<sup>4</sup>He 355 ratio is indeed due to an increased addition of He with a low <sup>3</sup>He/<sup>4</sup>He ratio to 356 the atmosphere (e.g., as a result of the mining and burning of fossil fuels), the 357  ${}^{4}\text{He}/{}^{20}\text{Ne}$  ratio would be expected to increase at a similar rate as the  ${}^{3}\text{He}/{}^{4}\text{He}$  ratio 358 decreases (dashed trend line in Fig. 4). This hypothesis cannot be ruled out based 359 on the observed  ${}^{4}\text{He}/{}^{20}\text{Ne}$  ratios. However, due to the large ratios of the masses 360 of <sup>4</sup>He and <sup>20</sup>Ne, the potential effect of effusion on the <sup>4</sup>He/<sup>20</sup>Ne ratio in the 1984 361 tank is large. Given this considerable uncertainty of the  ${}^{4}\text{He}/{}^{20}\text{Ne}$  ratio in the 1984 362 tank, we refrain from deriving further constraints of the atmospheric <sup>4</sup>He evolution 363 using our  ${}^{4}\text{He}/{}^{20}\text{Ne}$  data. 364

#### 365 5. Conclusions

Our noble gas analyses of 80 air aliquots taken from replicate subsamples of six CGAA tanks yielded robust and precise <sup>20</sup>Ne, <sup>40</sup>Ar, <sup>86</sup>Kr and <sup>136</sup>Xe concentra-

tions and <sup>3</sup>He/<sup>4</sup>He, <sup>20</sup>Ne/<sup>22</sup>Ne and <sup>40</sup>Ar/<sup>36</sup>Ar ratios in Cape Grim air during 1978– 368 2011. The noble gas composition of the originally sampled air is well preserved in 369 the CGAA. In contrast to the archives used in previous studies, potential artefacts 370 in the noble gas isotope composition resulting from sampling or storage are well 371 constrained from independent trace-gas monitoring data, and might be relevant 372 only in case of the 1984 tank. The noble gas record determined in the CGAA 373 therefore allowed us to determine the first systematic experimental evidence sup-374 porting the general assumption of stable Ne, Ar, Kr and Xe concentrations in the 375 atmosphere during the past few decades. 376

Our He isotope results provide strong evidence for a decrease of the atmo-377 spheric <sup>3</sup>He/<sup>4</sup>He ratio at Cape Grim during 1978–2011. The mean rate of decrease 378 amounts to  $(0.23 \pm 0.08)$ % per year, or to  $(0.30 \pm 0.08)$ % per year if a potential 379 effusion effect due to an assumed leak in the 1984 tank is included in the analysis 380  $(1\sigma \text{ errors})$ . These rates are consistent with many, but not all, previous determina-381 tions of the decrease of the atmospheric <sup>3</sup>He/<sup>4</sup>He ratio during the past few decades. 382 However, in contrast to previously measured decrease rates, our result is based on 383 a large and robust data set of <sup>3</sup>He/<sup>4</sup>He ratios measured in high-quality samples 384 of archived air which was always taken at the same location and under the same 385 wind conditions. Geographical variabilities in the atmospheric <sup>3</sup>He/<sup>4</sup>He ratio can 386 therefore be ruled out as a possible source of error in our analysis of the change 387 in the atmospheric  ${}^{3}\text{He}/{}^{4}\text{He}$  ratio. The decrease rate of the atmospheric  ${}^{3}\text{He}/{}^{4}\text{He}$ 388 ratio determined here therefore provides new and more robust constraints on the 389 evolution of the atmospheric <sup>3</sup>He/<sup>4</sup>He ratio during the past few decades. While 390 it was beyond the scope of our study to fully elucidate the sources and processes 39 resulting in the observed change of the <sup>3</sup>He/<sup>4</sup>He ratio, our result is consistent with 392

most predictions of the change in the atmospheric  ${}^{3}\text{He}/{}^{4}\text{He}$  ratio as a result from the mining and burning of fossil fuels.

To further investigate the nature and the source of the changing He isotope 395 composition in the atmosphere, it might be useful to further improve the analyt-396 ical precision of the <sup>3</sup>He/<sup>4</sup>He ratio (e.g., Sano et al., 2008; Mabry et al., 2010; 397 Jean-Baptiste and Fourré, 2012), as well as the temporal resolution of the time se-398 ries in the  ${}^{3}\text{He}/{}^{4}\text{He}$  and  ${}^{4}\text{He}/{}^{20}\text{Ne}$  ratios by analysing subsamples from additional 399 CGAA tanks. Combining precise and high-resolution time series of  ${}^{3}\text{He}/{}^{4}\text{He}$  and 400 <sup>4</sup>He/<sup>20</sup>Ne ratios are expected to yield further insights and quantitative constraints 401 with respect to the timing and the dynamics of the (possibly anthropogenic) sources 402 and processes resulting in the variability of the atmospheric He isotope composi-403 tion. 404

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Figures



**Figure 1:** Volumetric concentrations of <sup>20</sup>Ne, <sup>40</sup>Ar, <sup>86</sup>Kr and <sup>136</sup>Xe and isotope ratios <sup>20</sup>Ne/<sup>22</sup>Ne and <sup>40</sup>Ar/<sup>36</sup>Ar in Cape Grim Air Archive tanks (means and standard errors of the means as given in Tab. 3). The dashed extensions of the error bars in the 1984 data indicate the potential effusion effect in the 1984 tank (see text). *p* is the *p*-value resulting from a  $\chi^2$  test that the values plotted in each panel can be described by a common mean value, and *M* is the error-weighted mean of the data plotted in each panel. *p* and *M* were both calculated by (i) excluding or (ii) including the potential effusion effect in the 1984 data. Numbers next to the squares indicate the number of aliquots and subsamples (in parentheses) used to determine each data value.



**Figure 2:**  ${}^{3}\text{He}/{}^{4}\text{He}$  ratio observed in Cape Grim Air Archive tanks (means and standard errors of the means as given in Tab. 3). The dashed extension of the error bar in the 1984 value indicates the potential effusion effect in the 1984 tank (see text). Line A reflects the error-weighted mean value ('no trend' model excluding the potential effusion effect). Line B reflects least squares regression of a straight line ('linear trend' model excluding the potential effusion effect). Numbers next to the squares indicate the number of aliquots and subsamples (in parentheses) used to determine each data value.



**Figure 3:** Comparison of rates of decrease in the atmospheric  ${}^{3}\text{He}/{}^{4}\text{He}$  ratio reported in the literature (Tab. 1) and the rates determined in this work by (i) excluding or (ii) including the effusion correction of the data from 1984 tank in the regression of the trend line. Results are shown in chronological sequence of their publication. Black squares correspond to measured values, grey squares to modelled values. Error bars reflect standard errors (see notes in Tab. 1). The horizontal grey bar indicates the range of the rates determined in this work including their standard errors.



**Figure 4:**  ${}^{4}\text{He}/{}^{20}\text{Ne}$  ratio in Cape Grim Air Archive tanks (means and standard errors of the means as given in Tab. 3). The dashed extension of the error bar in the 1984 value indicates the potential effusion effect in the 1984 tank (see text). The dashed trend line indicates the linear trend resulting from the assumption that the rate of increase in the  ${}^{4}\text{He}/{}^{20}\text{Ne}$  ratio equals that of the decrease in the  ${}^{3}\text{He}/{}^{4}\text{He}$  ratio (calculated by excluding the potential effusion effect in the 1984 data; see text). Numbers next to the squares indicate the number of aliquots and subsamples (in parentheses) used to determine each data value.

Tables

**Table 1:** Summary of previously reported rates of decrease in the  ${}^{3}\text{He}/{}^{4}\text{He}$  ratio (*r*) and their standard errors, listed in chronological sequence of their publication.

Label	r	Descripton Ref.
	(% per year)	)
A	2.14±0.6	Comparison of absolute determinations of the <sup>3</sup> He/ <sup>4</sup> He ratios in Sano et al. (1988) three different air samples taken at Leningrad (1969), Ontario
		(1975 or earlier) and Tokyo (1988), each analysed in a different
_		laboratory (we assumed the reported error to reflect the $1\sigma$ level)
В	0.79±0.6	at different locations in Japan and in North America (California, USA) during 1977–1988 (we assumed the reported error to reflect the 1 $\sigma$ level)
С	-0.09+0.2	Trend analysis of ${}^{3}\text{He}/{}^{4}\text{He}$ ratios measured in 5 air samples taken Lupton and Gra-
C	0.0720.2	at different locations at the east coast of North America (Califor- ham (1991) nia, USA) during 1973–1990
$D_1$	-0.39±0.64	Comparison of absolute determinations of the <sup>3</sup> He/ <sup>4</sup> He ratios in Hoffmann and Nier
		four different air samples taken at Minneapolis (USA, 1956), (1993)
		Leningrad (1969), Ontario (1975 or earlier) and Tokyo (1988),
		each analysed in a different laboratory (we assumed the reported
р	0.27 + 0.97	error to reflect the $1\sigma$ level) Some as D, but evaluating the value determined from the sample Haffmann and Nier
$D_2$	$0.27\pm0.87$	same as $D_1$ , but excluding the value determined from the sample Hormann and Nier taken in Tokyo (1988) (1993)
Eı	$0.94 \pm 0.78$	Based on ${}^{3}\text{He}/{}^{4}\text{He}$ ratios measured in deep-water samples from Sano (1998)
-1		the South Pacific
$E_2$	0.28±0.15	Calculated by combining previously measured values Sano (1998)
$E_3$	0.33	Modeled value based on estimated He release from mining and Sano (1998)
		burning of fossil fuels (error was not estimated)
F	$0.14 \pm 0.07$	Modeled value based on estimated He release from mining and Pierson-Wickmann
		burning of fossil fuels (we assumed the reported error to reflect et al. (2001)
		the $1\sigma$ level). In the same study, "He/ He ratios in air inclusions
		of decrease in the ${}^{3}\text{He}{}^{/4}\text{He}$ ratio could be determined from these
		results.
$G_1$	$0.85 \pm 0.3$	Calculated from predicted He concentration increase from 1939 Lupton and Evans
		to 1981 resulting from mining and burning of fossil fuels (Oliver (2004)
		et al., 1984)
$G_2$	$0.05 \pm 0.03$	Trend analysis of 7 <sup>3</sup> He/ <sup>4</sup> He ratios measured in 7 air samples Lupton and Evans
		taken at different locations at the east coast of North America (2004)
C	0.00.005	(California and Oregon, USA) during 1973–2003
$G_3$	$0.00\pm0.05$	Same as $G_2$ , but using only the data from 5 samples, which were Lupton and Evans evaluated using a different gas standard (2004)
н	0 34+0 09	Trend analysis of ${}^{3}\text{He}/{}^{4}\text{He}$ ratios measured in air inclusions in Matsuda et al.
	0.51±0.07	porcelain samples originating from different locations in Japan (2010)
		and China, dating back to about 1400 AD, including a modern
		porcelain sample
$I_1$	$0.08 \pm 0.02$	Trend analysis of ${}^{3}\text{He}/{}^{4}\text{He}$ ratios measured in air inclusions in Sano et al. (2010)
		metallurgical slags originating from different locations in Japan,
_		dating back to about 900–1900 AD, and a modern air sample
I <sub>2</sub>	$0.00 \pm 0.03$	Same as $I_1$ , but the value of the <sup>3</sup> He/ <sup>4</sup> He ratio of the modern air Sano et al. (2010) sample was excluded from the evaluation

**Table 2:** Standard gas aliquots: relative standard deviations of the air standard results  $(\sigma_i^*)$  and assumed isotope composition of our air standard (see text;  $R_i^*$ : isotope ratios,  $C_i^*$ : volumetric concentration).

i	$\sigma^*_i$	$R_i^*$	$C_i^*$ (v/v)
<sup>3</sup> He/ <sup>4</sup> He	0.6%	1.399×10 <sup>-6</sup>	
<sup>4</sup> He/ <sup>20</sup> Ne	0.6%	0.318	
<sup>20</sup> Ne/ <sup>22</sup> Ne	0.1%	9.80	
<sup>40</sup> Ar/ <sup>36</sup> Ar	0.09%	$295.5^{\dagger}$	
<sup>20</sup> Ne	1.4%		$1.645 \times 10^{-5}$
<sup>40</sup> Ar	0.3%		$9.304 \times 10^{-3}$
<sup>86</sup> Kr	1.6%		$1.984 \times 10^{-7}$
<sup>136</sup> Xe	1.9%		$7.71 \times 10^{-9}$

<sup>†</sup>: For consistency with previous data measured in our noble gas laboratory, we use the  ${}^{40}$ Ar/ ${}^{36}$ Ar ratio recommended by the IUGS Subcommission on Geochronology (Steiger and Jäger, 1977) rather than the more recent value of 298.6 (Lee et al., 2006; Mark et al., 2011).

**Table 3:** Noble gas isotope ratios and concentrations in individual subsample aliquots (S: subsample number, A: gas amount in aliquot,  $\mu$ : means of values corresponding to a given tank,  $\sigma_{\mu}$ : standard errors of means). Missing values (NA) are due to technical problems during analysis or potential subsample contamination by He (see text).

S	Α	<sup>3</sup> He/ <sup>4</sup> He	<sup>4</sup> He/ <sup>20</sup> Ne	<sup>20</sup> Ne/ <sup>22</sup> Ne	<sup>40</sup> Ar/ <sup>36</sup> Ar	<sup>20</sup> Ne	<sup>40</sup> Ar	<sup>86</sup> Kr	<sup>136</sup> Xe
	$(cm_{STP}^3)$	$(\times 10^{-6})$				$(\times 10^{-5} v/v)$	$(\times 10^{-3} v/v)$	$(\times 10^{-7} v/v)$	$(\times 10^{-9} v/v)$
	Cape Grim Air Archive tank: 7.7.1978 (UAN: 780002)								
1	0.641	1.381	NĀ	9.793	295.2	1.62	9.26	2.00	7.58
1	0.323	1.409	0.3175	9.798	295.4	1.64	9.31	1.99	7.68
1	0.155	1.416	0.3172	9.799	295.2	1.64	9.33	1.99	7.52
1	0.627	1.394	0.3171	9.803	295.3	1.63	9.20	1.94	7.40
1	0.609	1.400	0.3161	9.801	295.2	1.65	9.23	1.97	7.88
2	0.548	1.394	0.3161	9.799	295.6	1.64	9.24	1.95	7.58
2	0.601	1.408	0.3187	9.814	295.7	NA	NA	NA	NA
2	0.265	1.419	0.3154	9.800	295.4	1.66	9.31	1.99	7.72
2	0.116	1.395	0.3157	9.797	295.5	1.67	9.39	1.97	7.76
2	0.047	1.379	0.3178	9.812	296.2	1.67	9.38	1.96	7.92
3	0.118	1.391	0.3206	NA	NA	1.64	9.37	1.97	7.57
4	0.567	1.389	0.3192	9.801	295.8	1.62	9.32	1.98	7.71
4	0.550	1.409	0.3181	9.808	295.6	1.65	9.39	2.01	7.90
4	0.526	1.407	0.3198	9.802	295.3	1.66	9.45	2.00	7.70
	μ:	1.399	0.3176	9.802	295.5	1.645	9.32	1.98	7.69
	$\sigma_{\mu}$ :	0.003	0.0004	0.002	0.1	0.004	0.02	0.01	0.04
			Cape G	rim Air Arch	nive tank: 2	3.5.1984 (UA	AN: 840004)		
1	0.598	1.393	0.3136	9.792	295.3	1.63	9.30	1.99	7.81
1	0.267	1.405	0.3131	9.800	295.8	1.64	9.36	2.01	7.69
1	0.106	1.401	0.3142	9.780	296.7	1.65	9.40	2.01	7.66
1	0.038	1.374	0.3173	9.795	NA	1.63	9.29	1.98	7.82
1	0.624	1.396	0.3122	9.798	295.7	1.68	9.38	2.01	7.73
1	0.600	1.404	0.3125	9.797	295.3	1.64	9.30	1.99	7.68
2	0.648	1.386	0.3140	9.796	295.5	1.63	9.27	1.97	7.59
2	0.334	1.400	NA	9.806	295.8	1.64	9.27	1.95	7.73
2	0.160	1.407	0.3136	9.795	294.7	1.64	9.35	1.85	7.68
2	0.071	1.399	0.3157	9.801	295.7	1.65	9.45	1.98	7.60
2	0.624	1.384	0.3136	9.787	295.7	1.65	9.25	1.97	7.86
2	0.313	1.394	0.3157	9.778	296.4	1.61	9.26	1.91	7.38
3	0.557	1.401	0.3125	9.787	295.8	1.61	9.19	1.98	7.70
3	0.534	1.403	0.3105	9.803	295.6	1.65	9.34	1.91	7.88
3	0.234	1.421	0.3104	9.775	296.1	1.62	9.32	1.89	7.55
3	0.226	1.417	0.3091	9.803	295.0	1.66	9.30	2.00	7.80
3	0.430	1.400	0.3101	9.792	295.7	1.64	9.30	2.05	7.83
3	0.401	1.397	0.3105	9.773	295.7	1.64	9.33	NA	NA

S	A	<sup>3</sup> He/ <sup>4</sup> He	<sup>4</sup> He/ <sup>20</sup> Ne	<sup>20</sup> Ne/ <sup>22</sup> Ne	<sup>40</sup> Ar/ <sup>36</sup> Ar	<sup>20</sup> Ne	<sup>40</sup> Ar	<sup>86</sup> Kr	<sup>136</sup> Xe		
	$(cm_{STP}^3)$	$(\times 10^{-6})$				$(\times 10^{-5} v/v)$	$(\times 10^{-3} v/v)$	$(\times 10^{-7} v/v)$	$(\times 10^{-9} v/v)$		
	μ:	1.399	0.3129	9.792	295.7	1.640	9.31	1.97	7.71		
	$\sigma_{\mu}$ :	0.003	0.0005	0.002	0.1	0.004	0.01	0.01	0.03		
	Cape Grim Air Archive tank: 2.3.1993 (UAN: 930279)										
1	0.530	1.388	0.3191	9.814	295.5	1.68	9.35	NA	7.62		
1	0.223	NA	0.3161	9.804	295.9	NA	NA	NA	NA		
1	0.244	NA	NA	9.792	295.5	NA	NA	NA	NA		
1	0.106	NA	0.3163	9.781	296.6	NA	NA	NA	NA		
1	0.116	NA	NA	9.788	295.1	NA	NA	NA	NA		
1	0.603	1.391	0.3166	9.803	295.6	1.63	NA	1.97	7.75		
1	0.293	1.405	0.3166	9.800	295.3	1.65	9.27	1.95	7.67		
1	0.165	1.410	0.3157	9.797	296.1	1.63	9.25	1.96	7.97		
1	0.088	1.409	0.3143	9.779	296.2	1.63	9.26	1.96	7.64		
1	0.060	1.386	0.3183	9.783	NA	1.66	9.33	1.99	7.38		
2	0.673	1.390	0.3156	9.797	295.6	1.64	9.28	2.00	7.76		
2	0.654	1.377	0.3176	9.815	295.5	1.63	9.28	2.00	7.78		
2	0.627	1.395	0.3174	9.783	295.5	1.63	9.29	2.01	8.02		
2	0.571	NA	0.3188	9.786	295.8	1.63	9.28	1.98	7.71		
2	0.559	NA	0.3157	9.795	295.8	1.65	9.31	1.99	7.71		
	μ:	1.395	0.3168	9.795	295.7	1.641	9.29	1.98	7.73		
	$\sigma_{\mu}$ :	0.004	0.0004	0.003	0.1	0.005	0.01	0.01	0.05		
			Cape G	rim Air Arch	hive tank: 1	.12.2004 (U	AN: 997089)				
1	0.565	NA	ŇĂ	9.801	295.5	1.65	9.33	1.97	7.66		
1	0.300	NA	NA	9.798	295.4	1.64	9.34	1.91	7.77		
1	0.137	NA	NA	9.791	295.7	1.65	9.34	1.98	7.72		
1	0.074	NA	NA	9.779	295.5	1.66	9.39	2.02	7.89		
1	0.611	NA	NA	9.796	295.4	1.65	9.25	1.98	7.53		
1	0.598	NA	NA	9.802	295.4	1.63	9.21	1.94	7.56		
1	0.575	NA	NA	9.803	295.2	1.65	9.25	1.97	7.52		
2	0.610	1.389	0.3209	9.795	295.4	1.65	NA	1.97	7.74		
2	0.590	1.388	0.3184	9.792	295.5	1.64	NA	1.98	8.05		
3	0.493	1.382	NA	9.798	295.6	1.64	9.38	1.95	7.92		
3	0.481	1.381	0.3216	9.789	295.2	1.65	NA	1.99	7.72		
3	0.181	1.407	NA	NA	295.4	NA	NA	NA	NA		
3	0.177	1.397	0.3179	9.797	295.9	1.65	NA	2.02	7.53		
3	0.170	1.382	0.3169	9.779	295.0	1.65	NA	1.94	7.76		
3	0.163	1.404	0.3160	9.818	294.7	1.64	NA	1.95	7.64		
3	0.064	1.382	0.3182	NA	NA	1.66	9.37	2.01	7.94		
3	0.233	1.393	0.3190	9.765	295.7	1.64	9.36	2.02	7.90		

**Table 3:** Noble gas isotope ratios and concentrations in individual subsample aliquots (continued).

S	Α	<sup>3</sup> He/ <sup>4</sup> He	<sup>4</sup> He/ <sup>20</sup> Ne	<sup>20</sup> Ne/ <sup>22</sup> Ne	<sup>40</sup> Ar/ <sup>36</sup> Ar	<sup>20</sup> Ne	<sup>40</sup> Ar	<sup>86</sup> Kr	<sup>136</sup> Xe	
	$(\mathrm{cm}_{\mathrm{STP}}^3)$	$(\times 10^{-6})$				$(\times 10^{-5} v/v)$	$(\times 10^{-3} v/v)$	$(\times 10^{-7} v/v)$	$(\times 10^{-9} v/v)$	
	<i></i>	1 391	0 3186	9 794	295.4	1 647	9 32	1 97	7 74	
	$\sigma_{\mu}$ :	0.003	0.0007	0.003	0.1	0.002	0.02	0.01	0.04	
	Cape Grim Air Archive tank: 16.12.2010 (UAN: 20101520)									
1	0.634	NA	NA	9.802	295.5	1.65	9.29	1.96	7.68	
1	0.317	NA	NA	9.805	295.3	1.65	9.26	1.96	7.92	
1	0.148	NA	NA	9.800	295.7	1.65	9.37	2.00	7.59	
1	0.066	NA	NA	9.807	297.0	1.65	9.39	1.99	7.88	
1	0.626	NA	NA	9.802	295.6	1.64	9.23	1.98	7.46	
1	0.342	NA	NA	9.802	295.2	1.64	9.33	1.98	7.54	
1	0.171	NA	NA	9.793	295.7	1.66	9.36	1.95	7.46	
1	0.082	NA	NA	9.792	295.4	1.66	9.34	1.97	7.67	
1	0.044	NA	NA	NA	296.5	1.68	9.46	2.01	7.85	
	μ:	NA	NA	9.800	295.8	1.652	9.34	1.98	7.67	
	$\sigma_{\mu}$ :	NA	NA	0.002	0.2	0.004	0.02	0.01	0.06	
			Cape Gr	im Air Arch	ive tank: 4.	5.2011 (UAN	N: 20110462	)		
1	0.606	1.401	0.3186	9.789	295.4	1.65	9.36	2.02	7.82	
1	0.605	1.387	0.3163	9.799	295.2	1.63	9.28	1.99	7.69	
1	0.590	1.383	0.3163	9.800	295.4	1.63	9.28	2.00	7.65	
1	0.567	1.383	0.3174	9.798	295.8	1.62	9.30	2.00	7.69	
2	0.623	1.383	0.3171	9.798	295.5	1.65	9.28	NA	NA	
2	0.604	1.387	0.3155	9.808	295.2	1.65	9.29	1.97	NA	
2	0.580	1.391	0.3171	9.794	295.9	1.66	9.34	1.97	7.72	
2	0.315	1.387	0.3145	9.814	296.0	1.62	NA	1.97	7.52	
2	0.301	1.408	0.3158	9.789	295.4	1.65	9.33	2.00	7.77	
	μ:	1.390	0.3165	9.799	295.5	1.640	9.31	1.99	7.70	
	$\sigma_{\mu}$ :	0.003	0.0004	0.003	0.1	0.005	0.01	0.01	0.04	

**Table 3:** Noble gas isotope ratios and concentrations in individual subsample aliquots (continued).