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

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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 10^6 yrs, with the potential exception of anthropogenic changes predicted for the He concentration and the $^3He/^4He$ 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 Cape Grim Air Archive, a well-defined archive of marine boundary layer air in the southern hemisphere. The resulting time series of the ^{20}Ne, ^{40}Ar, ^{86}Kr and ^{136}Xe concentrations and $^{20}Ne/^{22}Ne$ and $^{40}Ar/^{36}Ar$ ratios during 1978–2011 demonstrate the stability of the atmospheric Ne, Ar, Kr and Xe composition during this time interval. The He isotope data indicate a decrease in the $^3He/^4He$ during the same time interval at a mean rate of 0.23−0.30‰ per yr. This result is consistent with most model predictions of the rate of decrease in the atmospheric $^3He/^4He$ ratio associated with mining and burning of fossil fuels.

1. Introduction

The evolution of numerous trace gases in the terrestrial atmosphere (e.g., CO_2, CH_4, H_2, N_2O, CO, O_3, SO_2, nitrogen oxides, halocarbons) 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 atmosphere is generally assumed to be stable on a time scale of about 10^6 yr. There are no known sources or sinks that might modify the atmospheric inventory of these gases on this time scale (Ozima and Podosek, 2002), except for the degassing of radiogenic ^{40}Ar from the solid earth resulting in a very small increase in the atmospheric $^{40}Ar/^{36}Ar$ ratio by (0.066 ± 0.007)‰/Ma (Bender et al., 2008). In contrast, the concentrations of He isotopes in the atmosphere are governed by the dynamic balance of their sources and sinks, i.e., the accumulation of terrigenic He by outgassing of the solid earth, the contribution of extraterrestrial He, and the He loss into space (e.g., Kockarts, 1973; Lupton, 1983; Mamyrin and Tolstikhin, 1984). The mean residence time of He in the atmosphere is approximately 10^6 yr (Lupton, 1983; Mamyrin and Tolstikhin, 1984). The atmospheric He isotope concentrations resulting from the dynamic balance in the natural geological sources and sinks may be variable on time scales of about 10^5 years or more, but are assumed to be stable on a time scale of a few millennia (e.g., Lupton, 1983; Oliver et al., 1984; Mamyrin and Tolstikhin, 1984; Pierson-Wickmann et al., 2001).

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 in 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

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(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) 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 composition is, in analogy to the Suess effect for the carbon isotopic composition of atmospheric CO_2 (e.g., Tans et al., 1979), to analyse the $^3He/^4He$ ratio in archived air. The $^3He/^4He$ ratio in fossil fuels ($^6He/^4He \approx 10^{-8}–10^{-7}$; Ozima and Podosek, 2002) is commonly one to two orders of magnitude lower than the atmospheric ratio ($^3He/^4He = 1.40 \times 10^6$; Ozima and Podosek, 2002). The predicted decrease in the $^3He/^4He$ ratio associated with the mining and burning of fossil fuels should be detectable with currently available analytical methods, and is unaffected by chemical transformations of other gas species in the air archive.

Indeed, some studies reported experimental evidence for a decreasing $^3He/^4He$ ratio in the atmosphere during the past few decades (Sano et al., 1988, 1989; Sano, 1998, see Sec. 2 for an extended literature review). While this decrease in the $^3He/^4He$ ratio was interpreted in terms of an anthropogenic input of fossil-fuel derived He into the atmosphere (Sano et al., 1988, 1989; Sano, 1998), other studies questioned the existence of a change in the atmospheric $^3He/^4He$ ratio (Lupton and Graham, 1991; Hoffman and Nier, 1993; Lupton and Evans, 2004). In light of the resulting controversy on the He isotope composition of the atmosphere (Lupton and Graham, 1991; Hoffman and Nier, 1993; Sano et al., 1991), recent studies attempted to further constrain the potential change in the $^3He/^4He$ ratio on longer time scales by analysing the $^3He/^4He$ 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 heterogeneous sets of air samples taken at different locations. An effect of geographical differences in the atmospheric $^3He/^4He$ ratio could therefore not be ruled out (Sano et al., 1988, 1989, 2010; Jean-Baptiste and Fourré, 2012). In addition, the $^3He/^4He$ data obtained from the air inclusions in ancient porcelain and slags may be affected by the release of radiogenic He isotopes from the porcelain or the slags into the air inclusions (Pierson-Wickmann et al., 2001; Matsuda et al., 2010; Sano et al., 2010). Finally, the decrease rates of the $^3He/^4He$ ratio determined from the porcelain and slag samples depend strongly on poorly constrained assumptions on the timing and temporal evolution of the $^3He/^4He$ ratio in the atmosphere.

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 Section 2 and the recent review by Sano et al., 2013). 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 (except for the long-term increase in the $^{40}Ar/^{36}Ar$ ratio, Bender et al., 2008). 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 $^3He/^4He$ ratio as a proxy for environmental processes. For instance, the atmospheric $^3He/^4He$ ratio was discussed as a potential tracer to directly quantify the contribution of the mining and burning of fossil fuels to the accumulation of CH_4, CO_2 and possibly also other gases in the atmosphere (Sano, 1993; Sano et al., 2010). The atmospheric $^3He/^4He$ ratio might even allow studying the effect of enhanced groundwater ventilation, which might be linked to global warming (Pierson-Wickmann et al., 2001). Finally, better knowledge about the stability of the atmospheric noble gas composition would be highly useful to noble gas laboratories, because air is widely used as a standard gas for calibration of most noble gas analysis methods.

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

2. 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 $^3He/^4He$ ratio are summarised in Table 1.

Modelling studies have predicted an increase in the He concentration by 1–6‰ between 1939 and 1981 (Oliver et al., 1984), and a rate of decrease in the $^3He/^4He$ ratio during the past few decades of (0.14 ± 0.07)–(0.85 ± 0.3)‰ per yr (E_3, F and G_1 in Table 1; Sano, 1998; Pierson-Wickmann et al., 2001; Lupton and Evans, 2004).

Other potential He sources are the release of ^3He from radioactive decay of synthetic ^3H used in nuclear weapons (Lupton and Evans, 2004), and enhanced ventilation of terrigenic He from groundwaters due to the retreat of ice sheets and thawing of permafrost caused by global warming (Pierson-Wickmann et al., 2001). These two processes are not considered further here because their predicted rates of change in the atmospheric $^3He/^4He$ ratio are at least two orders of magnitude lower than those predicted from the mining and burning of fossil fuels.

Trend analyses of $^3He/^4He$ ratios measured in archived air or in the deep water of the South Pacific indicated rates of decrease in the atmospheric $^3He/^4He$ ratio in the range of (0.79 ± 0.6)–(2.14 ± 0.6)‰ per yr (A, B and $E_{1,2}$ in Table 1; Sano et al., 1988, 1989; Sano, 1998). However, results of other experimental analyses of $^3He/^4He$ ratios in air samples were interpreted to be consistent with a constant $^3He/^4He$ ratio in the atmosphere (C, $D_{1,2}$, $G_{2,3}$ in Table 1), and indicated the decrease in the atmospheric $^3He/^4He$ ratio during 1973–2003 to be less than 0.1‰ per yr at the 95% confidence level (Lupton and Graham, 1991; Lupton and Evans, 2004). This constraint is consistent with the decrease rate of the atmospheric $^3He/^4He$ ratio predicted by a recent mass-balance model (F in Table 1), but not with the higher rates determined from other models (E_3 and G_1) or measured data (A, B and $E_{1,2}$).

In recent studies (H and $I_{1,2}$ in Table 1), $^3He/^4He$ ratios measured in air inclusions in porcelain samples dating back to 1400 AD and in metallurgical slags dating back to 900 AD were