Chapter 2. Noble gases in the atmosphere

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The atmosphere is the primary terrestrial reservoir of the heavy noble gases (Ne, Ar, Kr, Xe) and precise knowledge of the isotopic composition of atmospheric noble gases is important for many – if not all – fields of noble gas geochemistry. Air noble gases, including helium, are very commonly used as a running laboratory standard for calibrating instrumental discrimination and sensitivity (see Chapter 1 of this volume), hence any potential temporal or spatial heterogeneities in the atmospheric noble gas composition could have consequences for the reliability and comparability of noble gas data. Metrological measurements such as the determination of Avogadro's constant and the gas constant also depend on accurate determination of the isotopic composition (and isotopic masses) of atmospheric noble gases. However, absolute isotopic measurements are not straightforward and this section reviews both how absolute isotopic determinations have been made and assesses the temporal and spatial variability of the atmosphere at the present and in the recent (<2 Ka) past.

Determination of the present-day atmospheric noble gas compositions

Absolute determinations of the atmospheric $^3He/^4He$

The terrestrial air contains He with a concentration of 5.24 ppm by volume (Gluckauf 1946; Gluckauf and Paneth 1946), considerably lower than would be predicted from solid-Earth degassing of radiogenic ^4He, because He escapes from the high temperature exosphere to inter-planetary space as a result of its light mass (Kockarts and Nicolet 1962) Helium is nevertheless supplied to the atmosphere by the solid Earth through volcanic activity (Craig, et al. 1975), fault movements, erosion and groundwater circulation (Sano, et al. 1998). The helium content and isotopic composition of the atmosphere are therefore the result of a balance between degassing from the mantle and crust, and escape of He isotopes to space. Since the residence time of He in the atmosphere is approximately 10^6 years (Torgersen 1989) and is significantly longer than the mixing time in the atmosphere of a few years (Tans, et al. 1989), the air $^3He/^4He$ ratio is believed to be constant on a global scale (Lupton 1983). On

this basis most laboratories engaged in helium isotope measurements use atmospheric helium as a natural isotopic standard (Lupton and Graham 1991). The ^{3}He/^{4}He ratios of terrestrial samples are usually expressed as a unit of Ra where Ra is the atmospheric ^{3}He/^{4}He ratio.

Aldrich and Nier (Aldrich and Nier 1948) were the first to measure the atmospheric ^{3}He/^{4}He ratio although their measurements were not calibrated against an absolute standard (i.e. pure ^{3}He and ^{4}He were not available); Coon (Coon 1949) also reported ^{3}He/^{4}He ratios of atmospheric and natural gases using neutron activation analysis where ^{3}He was detected by counting ionization pulses arising from the disintegration products of the reaction ^{3}He(n,p)^{3}H induced by thermal neutrons. Their measured atmospheric ^{3}He/^{4}He ratio was $(1.3\pm0.2)\times10^{-6}$, which agreed well with the value of $(1.2\pm0.2)\times10^{-6}$, reported by Aldrich and Nier (1948).

There are only three absolute ^{3}He/^{4}He measurements of atmospheric helium in the literature. In 1970, Mamyrin et al (Mamyrin, et al. 1970) reported that the atmospheric ^{3}He/^{4}He ratio in St. Petersburg, Russia, was $(1.399 \pm 0.013) \times 10^{-6}$ (1σ) and that air helium ratio did not vary with latitude, longitude, and altitude (up to 10 km) within the error margins of the individual measurements of about 2~3%. Clarke et al. (Clarke, et al. 1976) re-determined the atmospheric ^{3}He/^{4}He ratio in Ontario, Canada. The value of $(1.384 \pm 0.006) \times 10^{-6}$ (1σ) was somewhat lower but in agreement, within error, of the St Petersburg value. The average of the two measurements, 1.39×10^{-6} was accepted as the air ^{3}He/^{4}He ratio until the end of 1980s when Sano et al. (Sano, et al. 1988) determined an atmospheric ^{3}He/^{4}He ratio of $(1.343 \pm 0.013) \times 10^{-6}$ (1σ) at Ueno Pak, central Tokyo, Japan. This value was apparently lower than the previous data. Either experimental artifacts and/or natural phenomenon accounted for the difference. The International Union of Pure and Applied Chemists (IUPAC) committee currently uses Sano et al's value $(1.343 \pm 0.013) \times 10^{-6}$). In 1990, Davidson and Emerson (Davidson and Emerson 1990) measured the absolute ^{3}He content of air by mass spectrometry. When combined with an earlier measurement of the atmospheric ^{4}He abundance (Holland and Emerson 1987), this provides an additional estimate of the atmospheric ^{3}He/^{4}He ratio of $(1.393 \pm 0.014) \times 10^{-6}$ (1σ). The average of the above determinations taking into their weighted errors is $(1.382\pm0.005) \times 10^{-6}$ (1σ) and this is likely the best estimate of atmospheric helium isotopic composition (Ra) for the period 1970-1990.

It should also be noted that Matsuda et al. (Matsuda, et al. 2002) have prepared an artificial mixture of ^{3}He and ^{4}He to be used as an internal standard for precise measurements of mantle-derived samples and for cosmogenic dating. Since He is depleted in air and the isotopic composition is low compared with mantle-derived or cosmogenic samples, a large volume of air is needed to obtain an adequate ^{3}He signal in the mass spectrometer, creating purification difficulties. It is in any case preferable to have the composition of the standard as close as possible as the samples. As a result, an artificial standard with a high ^{3}He/^{4}He ratio was required. The standard prepared for the purpose is called the "He Standard of Japan" (HESJ) and the recommended ratio is 20.63±0.10 Ra (1σ) calculated by the weighted mean of six independent determinations relative to air in four noble gas laboratories.

Absolute measurements of atmospheric Ar isotope ratios

Of all the noble gases, accurate determination of the atmospheric Ar isotopic composition is probably the most important; not only is Ar the most abundant atmospheric noble gas but is certainly the most measured noble gas. For example, the K-Ar and Ar-Ar methods for dating rocks and minerals depend on knowledge of the atmospheric ^{40}Ar/^{36}Ar and ^{40}Ar/^{38}Ar ratios for mass discrimination corrections (Turrin, et al.) and for correcting for atmospheric contamination.

The atmospheric Ar isotope ratio was originally reported in a seminal paper by Nier (Nier 1950a) and has more recently been revisited by two independent studies. Absolute isotope determinations consist of creating reference gases with known isotopic ratios by mixing known quantities of the pure (or as near pure as possible) isotopes. The reference gases are then used in order to characterize instrumental mass fractionation (IMF) in the mass spectrometer. Once the IMF is well known then the unknown (atmospheric Ar) can be measured and corrected for the mass spectrometer fractionation in order to estimate the true isotope composition.

Nier (Nier 1950a) mixed isotopically pure ^{40}Ar and ^{36}Ar produced by selective thermal diffusion; the respective quantities were determined volumetrically. The discrimination of two different mass spectrometers (MS1 and MS2) were constrained using four mixtures with different ^{40}Ar/^{36}Ar ratios; this mass discrimination was measured at 1.6 ±0.3 per mil per mass unit for the MS1 mass spectrometer (the more accurate of the two mass spectrometers). Nier measured values of 295.5 ±0.5 (1σ) and 0.1880 ± 0.0003 for ^{40}Ar/^{36}Ar and ^{38}Ar/^{36}Ar

respectively on laboratory air (dried over hot lithium metal); commercially available gas (Air Reduction Sales Corporation) was also analyzed but found to be fractionated (depleted in [36]Ar and [38]Ar relative to air).

The isotopic composition of air was re-investigated in 2006 by Lee et al (Lee, et al. 2006) who used considerably more precise gravimetric methods to constrain the masses of the isotopic mixtures, and used multicollection mass spectrometry (a MAT271 gas source mass spectrometer) to better constrain the discrimination and isotopic ratios. Lee et al proposed $(^{40}Ar/^{36}Ar)_{air} = 298.6 \pm 0.3$ (1σ) and $(^{38}Ar/^{36}Ar)_{air} = 0.1885$. Most recently, Valkiers et al (2008) using a similar methodology to Lee et al (gravimetric mixtures but starting with different gases) confirmed the redetermined $^{40}Ar/^{36}Ar$ value (obtaining a value of 298.7 ±0.1) but disagreed for the $(^{38}Ar/^{36}Ar)_{air}$ measurement, finding a value of 0.1898 ±0.0001.

Without constraining the IMF, Mark et al (Mark, et al.) recently measured $^{40}Ar/^{36}Ar$ and $^{38}Ar/^{36}Ar$ on different air aliquots reasoning that since IMF results in mass-dependent fractionation, then the true atmospheric isotopic composition should lie on the mass fractionation line (the slope defined by $\sqrt{(40-36)/(38-36)}$) passing through the raw (non-IMF corrected) mass spectrometer data. Assuming that this hypothesis is correct, it would appear to confirm that the Lee et al (2006) measurements are the best estimate of modern air (Figure 1),

It is important to note that commercial processing of air can fractionate Ar isotopes: Valkiers et al (2008) observed a spread in $^{40}Ar/^{36}Ar$ of ~1% in commercial sources of Ar produced by distilling air. However, Mark et al (2011) found no difference between commercial Ar (produced by distilling air) and locally sampled air. Similar variations have been observed for Ne isotopes (Pavese, et al. 2005). Mass fractionation for distilled gases depends in fact on the distillation process itself and may vary from tank to tank.

Absolute measurements of Ne, Kr and Xe isotopic compostions.

Nier (Nier 1950b) determined the isotopic compositions of Ne, Kr and Xe in the atmosphere using the same mass spectrometer (MS1) as that used for the air Ar isotope measurements see above). Mass discrimination was estimated either by using the $^{36}Ar^{++}/^{40}Ar^{++}$ ratio (for Ne) or assuming that the mass discrimination in the spectrometer for Ar (which was accurately determined using synthetic mixtures of ^{36}Ar, ^{38}Ar and ^{40}Ar) applied to all the heavy noble gases: individual isotopes were not available for the other noble gases, preventing direct determination of mass discrimination for each element. The Ne isotopic

composition of air was re-determined by (Eberhard.P, et al. 1965) and was found to be essentially identical to Nier's measurement.

The Ne, Kr and Xe isotopic measurements by Nier in the late 1940's (Nier 1950b) have not changed since, although the errors have been reduced by modern redeterminations (Table 1): the fact that these values are still valid over 60 years after their determination are testament to a highly skilled analyst.

Subsequent absolute determinations of the Ne, Kr and Xe isotopic compositions have been made by the Institute for Reference Materials and Measurements (IRMM) group, Geel, Belgium (Aregbe, et al. 1997; Aregbe, et al. 1998; Aregbe, et al. 1996b; Valkiers, et al. 1998); these measurements are currently used by IUPAC (LAETER, et al. 2003)as the best estimates for atmospheric Kr and Xe isotopic composition. The IRMM approach is to prepare synthetic volumetric or gravimetric mixtures of gases from single isotope gases in order to calibrate instrumental mass fractionation in the MAT271 mass spectrometer used for the determinations (e.g. near-pure ^{86}Kr was added to atmospheric Kr to create known variable isotope ratios). Potential diffusive fractionation of Kr and Xe isotopes during sample inlet were monitored and corrected for (and found to deviate from ideal gas behavior by only a few ppm). Bottles of Kr and Xe were prepared from purified air (by the Messer Greisheim company) which were then calibrated and certified as primary isotope gas standards by IRMM (IRMM-2030 for Kr and IRMM-2000 for Xe), with traceable and certified isotopic compositions (Aregbe, Valkiers, Mayer and DeBievre 1996b).

Concerning the atmospheric Ne isotope compositions IUPAC refers to a 1984 paper by Bottomley (Bottomley, et al. 1984) and not the IRMM study (Valkiers, et al. 2008). Table 1 provides both the IUPAC preferred values and the more recent IRMM determinations, which differ from IUPAC only in the measurement uncertainty

Thus it appears that the atmospheric compositions of Ne, Ar, Kr and Xe have been well calibrated and for Ar, Kr and Xe there are reference materials available for laboratories interested in making SI-traceable determinations. Nevertheless, all the measurements were made on commercially produced gases (made by distilling air) supplied by Messer which could have systematic offsets relative to air; this has been established for the case of neon

(Pavese, Fellmuth, Head, Hermier, Hill and Valkiers 2005). It should be noted that most laboratories normalize their analyses to the quoted atmospheric values and essentially report only relative isotope ratio variations, therefore the potential errors in reported data (which are only relative isotope shifts and not absolute measurements) are relatively minor.

Table 1 IUPAC approved noble gas isotopic compositions of the atmosphere (LAETER, BÖHLKE, BIÈVRE, HIDAKA, PEISER, ROSMAN and TAYLOR 2003)

Element	Dry air abundance, ppmv*	Isotope	IUPAC	Alternative	comments
Helium	5.24	^{3}He	0.000 001 34(3)	0.000 001 382 (5)	IUPAC = Sano et al ; Alternative = average (see text)
		^{4}He	0.999 998 66(3)	0.999 998 62(36)	
Neon	18.18	^{20}Ne	0.9048(3)	0.90472(14)	Essentially the values determined by Nier although a reference is given to Bottomley (Bottomley, Ross and Clarke 1984). Alternative calibration from (Valkiers, et al. 1994)
		^{21}Ne	0.0027(1)	0.00266(26)	
		^{22}Ne	0.0925(3)	0.09262(26)	
Argon	9,340	^{36}Ar	0.003 365(30)	0.003 336(4)	IUPAC considers Nier's values most reliable due to uncertainties on 38Ar; Lee et al (Lee, Marti, Severinghaus, Kawamura, Yoo, Lee and Kim 2006) chosen as alternate because of confirmation by Mark (Mark, Stuart and de Podesta 2011)
		^{38}Ar	0.000 632(5)	0.000 629 (1)	
		^{40}Ar	0.996 003(30)	.996 035 (4)	
Krypton	1.14	^{78}Kr	0.003 55(3)		(Aregbe, Valkiers, Mayer and DeBievre 1996b)
		^{80}Kr	0.022 86(10)		
		^{82}Kr	0.115 93(31)		
		^{83}Kr	0.115 00(19)		
		^{84}Kr	0.569 87(15)		
		^{86}Kr	0.172 79(41)		
Xenon	0.09	^{124}Xe	0.000 952(3)		IUPAC data from (Valkiers, Aregbe, Taylor and De Bievre 1998)
		^{126}Xe	0.000 890(2)		
		^{128}Xe	0.019 102(8)		
		^{129}Xe	0.264 006(82)		
		^{130}Xe	0.040 710(13)		
		^{131}Xe	0.212 324(30)		
		^{132}Xe	0.269 086(33)		

| | | ^{134}Xe | 0.104 357(21) | | |
| | | ^{136}Xe | 0.088 573(44) | | |

*ppmv: parts per million by volume fraction ≈ parts per million by mole fraction

Heterogeneity of the modern atmosphere

Possible temporal variation of atmospheric helium isotopes

Oliver et al. (Oliver, et al. 1984) carefully measured and reported the He concentration in the Earth's lower atmosphere. The value of 5.222±0.017 ppm by volume (1σ) agrees well with the certificated number of 5.239±0.004 ppm (1σ) determined by Gluckauf (Gluckauf 1946). Although the He contents are identical, Oliver et al. (1984) suggested that (3 - 12) x 10^{16} ccSTP of He had been released into the atmosphere from natural gas production between 1939 and 1981. This anthropogenic He should have increased the 1981 inventory of atmospheric He by 0.1 – 0.6% compared to Gluckauf's 1946 determination, even though the excess was not detectable in their measurements. Stimulated by this work, Sano et al. (Sano, et al. 1989) measured the ^{3}He/^{4}He ratios of 20 air samples at several different sampling sites and dates. There was a possible change of the atmospheric helium isotope ratio from 1.362×10^{-6} in December 1977 to 1.339×10^{-6} in September 1988, or a decrease in ^{3}He/^{4}He of about 0.74‰/year. Although this change could be attributed to local/non-global effects or experimental artifacts, the observations are also consistent with a significant anthropogenic release of crustal He with low ^{3}He/^{4}He ratio (~3×10^{-8}). Lupton and Graham (Lupton and Graham 1991) countered that this estimated rate of decrease in ^{3}He/^{4}He was not statistically different from a zero time rate of change (TROC). They also reported California marine air data which showed a TROC of (+0.09±0.43)‰/year (2σ), i.e. that there was no evidence that the atmospheric He isotope ratio is changing with time. Sano et al. (Sano, et al. 1991) re-evaluated the original Sano et al. data and reported a non-zero TROC of (-0.81±0.62)‰/year (2σ). Taking into account the TROC of three independent determinations (Davidson and Emerson 1990; Mamyrin, Anufriyev, Kamenskiy and Tolstikhin 1970; Sano, Wakita, Makide and Tominaga 1989) as well as that of Lupton and Graham, the conclusion of Sano et al.

(1991) was that the average TROC based on laboratory measurements of contemporary air was (-0.245±0.055)‰/year (2σ).

Hoffman and Nier (Hoffman and Nier 1993) reported an absolute helium isotopic ratio which was measured by a double focusing mass spectrometer in November 1956. Their value of (1.371±0.019)x10^{-6} (2σ), when combined with the previously reported results above, effectively extending the integration time to a 32 year period, gave a regression line corresponding to a TROC of (-0.3±8.7)‰/year (2σ). Sano (Sano 1998) reported a TROC of (-0.9±1.6)‰/year (2σ) based on the comparison between GEOSECS Pacific Expedition ^{3}He/^{4}He data (Site 263 and 251) which was calibrated against California marine air collected in 1973 (Lupton and Graham 1991) and South Pacific deep seawater values (SA-7 and SA-6 of Sano et al. (Sano, et al. 1995)) against air from Chiba, Japan in August 1992.

Pierson-Wickman et al. (Pierson-Wickmann, et al. 2001) measured the isotopic composition of He trapped in historical metallurgical slag from France and the United Arab Emirates in an attempt to investigate variations in the atmospheric ^{3}He/^{4}He ratio with time. Iron is manufactured through the oxydo-reduction of Fe-ore reduced over charcoal with air being pulsed and circulated through the furnaces. The best results in terms of sample reproducibility was obtained for blast furnaces that appeared during the Middle Age in which the temperatures reached 1,600°C and the mass of circulated air was comparable to the mass of processed Fe ore, assuring efficient ventilation and therefore noble gas exchange with air. Air was trapped in 0.1-1 mm size vesicles contained in the slag matrix having a composition of forsterite therefore with negligible helium diffusivity at environmental temperatures. Pierson-Wickman et al. found that the He isotopic composition of air trapped in vesicles from industrial slags from the Middle Age and from the beginning of the 20th century was 30±12‰ (at 95 % conf. level) higher than Today. They considered various natural sources and sinks of He isotopes in the period concerned and concluded that these could account for this significant change in atmospheric ^{3}He/^{4}He. Thus they concluded that crustal helium rich in radiogenic ^{4}He has been released to the atmosphere due to industrial activities (mostly mining and hydrocarbon exploitation), and that the inferred fluxes from anthropogenic activity were consistent with the observed variation. They suggested a TROC of (-0.14±0.07)‰/year (2σ).

Lupton and Evans (Lupton and Evans 2004) compared the ^{3}He/^{4}He ratio of samples of Pacific marine air collected over the 30-year period from 1973 to 2003 against a secondary geothermal gas standard and also against a running air standard. They concluded that the rate of change of air ^{3}He/^{4}He over the past 30 years fell between –0.10 and +0.02‰/year, which is a TROC of (-0.042±0.061)‰/year. Figure 2 shows the compilation of the time rate of atmospheric ^{3}He/^{4}He change in the literature. When we take into account all TROCs, the weighted mean of the various estimates is (-0.086±0.045)‰/year (2σ). This value is apparently distinct from the zero rate of change, even though it corresponds to only 2.6‰ change in the atmospheric ^{3}He/^{4}He ratio over the past 3 decades, which is below the detection limit of most laboratories in the world.

Very recently Matsuda et al. (Matsuda, et al. 2010) reported that the ^{3}He/^{4}He ratios in some old Chinese porcelain were significantly higher than the present-day air value. They claimed that porcelain can be used as a paleo-atmosphere time capsule over historical times. Taking into account their data, the average ^{3}He/^{4}He ratio is 1.516±0.043 x 10^{-6} (1σ, assuming that present Ra = 1.382x10^{-6} from Table 1) at 1400AD and 1.447±0.030 x 10^{-6} (1σ) at 1700AD. They took an average of both data, 1.476±0.025 x 10^{-6} (1σ) as a pre-1700AD atmospheric value (i.e before the Industrial Revolution) and suggested a TROC of (-0.34±0.18)‰/year (2σ) under the assumption that the air ^{3}He/^{4}He ratio decreased linearly during the 200 years since the middle of the 18 century to 1970AD. This TROC is significantly larger than the average TROC of (-0.086±0.045)‰/year (2σ) as calculated in the above discussion.

Sano et al. (Sano, et al. 2010) have reexamined the ^{3}He/^{4}He ratios of air presumed to be trapped in historical metallurgical slag derived from Japan. They observed that it is difficult to use the Ra unit when discussing a possible temporal variation of the air ^{3}He/^{4}He ratio (because this is Ra itself!) but instead expressed the data relative to the He Standard of Japan (HESJ; see above). The mean ^{3}He/^{4}He ratio of gases extracted from metallurgical slag found at refineries in operation between AD1603 and 1907 in Japan was (5106±108) x 10^{-5} R_{HESJ} (2σ) and was consistent with the reported value of (5077±59) x 10^{-5} R_{HESJ} in historical slags from France and United Arab Emirates (Pierson-Wickmann, Marty and Ploquin 2001).

These values are about 40‰ higher than that of average modern air (4901±4) x 10^{-5} R_{HESJ} from AD 2006 to 2008 (this value is obtained by the average of air samples with various locations as discussed below).

Anthropogenic sources of atmospheric helium

All slag ^{3}He/^{4}He data as well as porcelain are plotted against the year together with the modern air value in Figure 3 (top panel). When we assume all data are correct, the simple linear regression taking into account the weight of each experimental error yields a slope of – (0.41±0.11)x10^{-5} R_{HESJ} /year (2σ), which is equivalent to a TROC of (-0.084±0.022) ‰/year (2σ). Since the uncertainty in the composition of the modern surface air, (4901±4) x 10^{-5} R_{HESJ}, is significantly smaller than that of slag and porcelain samples, the regression line should be forced to pass through the point of the air value in Figure. 4a. The resulting TROC is identical to the weighted mean of data, (-0.086±0.045) ‰/year in Fig. 2.

It is possible that the decrease of the air ^{3}He/^{4}He ratio is due to a natural perturbation of the steady-state atmosphere resulting from the geomagnetic reversal at 0.79-0.76 Ma (Izett and Obradovich 1994) which probably severely depleted air helium at that time and the atmosphere is now slowly returning to equilibrium (Kockarts 1973; Sano, Wakita, Makide and Tominaga 1989). Pierson-Wickmann et al (Pierson-Wickmann, Marty and Ploquin 2001) suggested that degassing of the solid Earth could have been increased by a factor of 10 since the last deglaciation (15,000 yrs ago) due to recirculation of groundwater in previously frozen areas which accumulated radiogenic He while frozen, then release this during melting. Similarly, melting of glaciers that might have accumulated crustal ^{4}He could increase the rate of ^{4}He release to the atmosphere during post-glacial times. Therefore the TROC of -0.086‰ /year may be attributable to natural processes.

In addition to natural processes, anthropogenic He sources to a non-steady-state atmosphere should be taken into account (Oliver, Bradley and Farrar 1984). Possible sources and sinks of atmospheric He (from (Sano, Furukawa and Takahata 2010)) were estimated and are listed in Table 2. Commercial production of He gas for cryogenic purposes, welding and

space missions was 7.6 x 10^9 mol/year in 2006 (US Geological Survey. 2009, http://minerals.usgs.gov/minerals/pubs/commodity/helium). This value is ten times greater than the natural crustal degassing rate of 6.1x10^8 mol/year (Ozima and Podosek 1983), clearly indicating that there are likely anthropogenic sources of He in the atmosphere.

Table 2 Possible sources and sinks of atmospheric helium

	^{4}He (mol/year)
Total inventory	9.3x10^{14} (a)
Source	
Natural flux	
Degassing of solid Earth	6.1 x 10^8 (a)
Recirculation of groundwater	6 x 10^9 (b)
Fossil fuel flux (in 2006)	
Grade-A Helium Production	7.6 x 10^9 (c)
Natural Gas	1.3 x 10^{11}
Petroleum	2.1 x 10^{11}
Total	3.4 x 10^{11}
Sinks	
Escape (Thermal and Non-thermal)	8.3 x 10^8 (a)

(a): from Ozima and Podosek (1983); (b): from Pierson-Wickmann et al (c): from U.S. Geological Survey (2009)

A further major source of crustal He can be attributed to fossil fuel exploitation (Pierson-Wickmann, Marty and Ploquin 2001; Sano, Wakita, Makide and Tominaga 1989). Consumption of natural gas, petroleum and coal have been well documented by the Carbon Dioxide Information Center (http://cdiac.ornl.gov). It is reasonable to assume that the rate of consumption of fossil fuel is similar to that of production on a global scale. However, the He content of fossil fuel is known to be highly variable and difficult to constrain. Based on ~3000 analyses of natural gas samples containing less than 8% He in the U.S.A., Zartman et al. (Zartman, et al. 1961) reported that the He abundance showed a log-normal distribution with a mean concentration of 0.217 volume %. The mean He content in natural gas from

outside the U.S.A. is not well documented, but might be 0.1 % (Oliver, Bradley and Farrar 1984). The He/total C molar ratio of crude oil in the Paris basin, France was 800ppm (Pinti and Marty 1995). On the other hand, there is no available datum in coal samples. We assume the He/C ratio of 7×10^{-11} for coal (an average U content = 2 ppm for coal, Th/U = 4 (Swaine and Goodarzi 1997) and an average age of coal of 360 Ma). Thus ^{4}He from coal is probably negligible.

It is then possible to calculate the anthropogenic release of crustal He due to fossil fuel production (see Table 2), resulting in a total fossil fuel flux of 3.4×10^{11} mol He/year in 2006, which is 3 orders of magnitude larger than the natural flux. On the other hand, the monotonous decrease of atmospheric ^{3}He/^{4}He ratio (the trend in Fig. 3a), i.e. a TROC of -0.084 ‰/year implies a He input to the atmosphere at 8×10^{10} mol/year based on the simple mass balance calculation where crustal He has a ^{3}He/^{4}He ratio of 3×10^{-8} (Mamyrin and Tolstikhin 1984). Thus the He flux estimated from the global fossil fuel production statistics is about 4 times higher than the TROC calculation.

From the He content in natural gas and petroleum as stated above, it is possible to simulate the secular variation of the atmospheric ^{3}He/^{4}He ratio (based on the fossil fuel consumption per year from AD 1751 to 2006 supplied by the Carbon Dioxide Information Analysis Center (http://cdiac.ornl.gov)). Little change is expected between AD 1400 and 1751 because of minimal consumption and/or production of fossil fuel compared to after the Industrial Revolution. The solid black curve in Fig. 3b shows the calculated change in atmospheric ^{3}He/^{4}He ratio together with observed slag and porcelain data. All data except for the Chinese porcelain in 1400AD (2nd crushing of POR2 in Matsuda et al. (Matsuda, Matsumoto and Suzuki 2010)) are consistent with the calculated ^{3}He/^{4}He change within the error margins resulting from uncertainties in He/C ratios, suggesting that the simulation is valid. However the simulation predicts an average decrease at 0.32‰/year for the last 10 years, significantly higher than the TROC value of -0.086±0.045‰/year obtained by measuring contemporary air (Fig. 2). In reality, the true TROC is probably located between the monotonic decrease in the atmospheric ^{3}He/^{4}He ratio (dotted line in Fig. 3a) and the recent catastrophic decrease (a solid curve in Fig. 3b). Even so, taking the largest variation of

0.32‰/year, this is still below the detection capabilities of most laboratories. Thus atmospheric He is still suitable as a laboratory standard.

Possible spatial variation of atmospheric helium isotopes

Changes of the atmospheric $^3He/^4He$ ratio with latitude and longitude were assessed by the pioneering work of Mamyrin et al. (Mamyrin, Anufriyev, Kamenskiy and Tolstikhin 1970). They reported that the spatial variation with both location and altitude (up to 10km) was within the error margin of individual measurements of about 3%. More recently Sano et al. (Sano, Furukawa and Takahata 2010) measured the $^3He/^4He$ ratios of 21 surface air samples collected around the world with a precision of 2-4‰ (2σ) using a newly developed analytical system (Sano, et al. 2008). Even though the data available are not sufficient to cover the entire planet, the sites cover high, low and mid latitudes (ranging from Svalbard, Norway, to far Showa base, Antarctica). The atmospheric $^3He/^4He$ ratios generally increase from north to south (Figure 4a), but they do not change significantly from east to west (Fig. 4b). The result is attributable to the fact that mixing of long-lived tracers between northern and southern hemispheres is a much slower process than east to west transport (Jacob 1999; Muller and Brasseur 1995).

By fitting the atmospheric $^3He/^4He$ ratios variation with latitude by eye (dotted curve in Fig. 4a), one obtains an apparently constant $^3He/^4He$ ratio from 38˚S to 38˚N, with high values in Antarctica and low values at high latitudes in the northern hemisphere (from 38˚N to 46˚N). When we take the uniform $^3He/^4He$ ratio in mid-latitudes, the average becomes $(4901\pm4) \times 10^{-5}$ R_{HESJ}, which could be adopted as a representative value of the present atmosphere (see the end of section 2.2.4). This would result in a $^3He/^4He$ ratio in HESJ of 20.404 ± 0.017 (2σ) in Ra units. There is a relatively high $^3He/^4He$ ratio in Antarctica but not in the Arctic. The major source of atmospheric ^3He is auroral precipitation into the upper atmosphere in polar regions (Johnson and Axford 1969). Therefore, these higher $^3He/^4He$ ratios may be attributable to the auroral effect, but the apparently lower ratio in the Arctic needs to be investigated further.

The average ^{3}He/^{4}He ratio of air samples at high latitudes from 38°N to 46°N is (4886±7) x 10^{-5} R$_{HESJ}$ (2σ), 0.31±0.14% lower than the average value of (4901±4) x 10^{-5} R$_{HESJ}$, although there is a possibility of experimental artifacts in Sano et al. (Sano, Furukawa and Takahata 2010). The atmospheric volume at high latitudes (38°N~ 46°N) is calculated to be about 5.2% of the global atmosphere, assuming that the volume is proportional to surface area. The He inventory of the region is estimated to be 4.8x10^{13} mol, (5.2 % of the total inventory of 9.3x10^{14} mol (Ozima and Podosek 1983)). In order to make the regional atmospheric ^{3}He/^{4}He ratio 0.31±0.14% lower than the mid-latitude helium, a local input of crustal He of (1.5±0.7)x10^{11} mol is required. This amount is significantly smaller than a single year of anthropogenic He (5.9x10^{11} mol y-1). Because atmospheric circulation and mixing homogenize the atmosphere (Jacob 1999), the released anthropogenic He could rapidly dissipate, causing the air ^{3}He/^{4}He to be higher than expected. Note that the 0.31±0.14% anomaly is below the detection limit of most noble gas laboratories in the world.

Anthropogenic Kr and Xe

Fission of nuclear fuel produces Xe and Kr that are isotopically distinct from that of the atmosphere, the precise isotopic pattern depending on the fuel characteristics and subsequent operation of the nuclear pile. Weiss et al (Weiss, et al. 1986) demonstrated that the atmospheric ^{85}Kr (t1/2 = 10.73 years) budget is dominated by ^{85}Kr produced during fission. Aregbe et al (Aregbe, et al. 1996a) modeled the stable Kr and Xe isotopes expected from mixtures between air and Kr and Xe produced by two different nuclear pathways: from civil nuclear energy production in a Pressurized Water Reactor (PWR) and from plutonium enrichment. However, the lower fission yields and higher atmospheric abundance of Kr means that stable Kr isotopes are not particularly suited to tracing nuclear atmospheric inputs. Normalising to ^{132}Xe, Agrebe et al considered that the most sensitive Xe isotopes for tracing fission produced Xe are ^{136}Xe/^{132}Xe and ^{129}Xe/^{132}Xe with production ratios greater and lower than atmosphere respectively (however, it would seem more logical to the authors of this chapter to normalize to ^{130}Xe as this is nearly completely shielded); Pu-enrichment and UOX (PWR) produce characteristically different Xe isotope patterns. Aregbe et al (Aregbe, Mayer, Valkiers and DeBievre 1996a) compared the calculated isotope anomalies generated by 1 g of fission Xe variably diluted by air Xe with the (impressive) measuring capacity of the MAT

271 mass spectrometer at IRMM, Belgium to detect Xe isotope anomalies (about 0.02 permil for both $^{129}Xe/^{132}Xe$ and $^{136}Xe/^{132}Xe$). They concluded that 1g of fission Xe diluted in 10^8 m3 of air (~10^8 kg air) would be detectable, and at 1g fission Xe in 10^6 m3 of air it would be possible to distinguish between uranium processed for civil or weapons purposes. Thus Xe isotopes have the possibility for identifying nuclear activity if air samples are available close to the reactor. Nevertheless, anthropogenic Xe is highly unlikely to have affected the isotopic composition of atmospheric Xe, given an atmospheric mass of the order 5 x10^{18} kg and an annual global U production of the order 50 x10^6 kg (2009 data: source: "World Uranium Mining". World Nuclear Association.), approximately 1000 years of U extraction would be required in order to create a measurable excess in the global $^{136}Xe/^{132}Xe$.

Temporal variation of atmospheric argon isotopes

Apart from helium, argon is the only other noble gas for which temporal variations have been reported. Argon has three natural stable isotopes, ^{36}Ar, ^{38}Ar and ^{40}Ar with well measured relative abundances (see Table 1). While the first two are primordial, that is, have been trapped from one or several cosmochemical reservoirs when the Earth formed. There was virtually no ^{40}Ar at that time and this isotope was produced in the silicate Earth (mantle and crust) by the decay of radioactive ^{40}K. Thus ^{40}Ar accumulated in the atmosphere due to magmatic and tectonic degassing of the mantle and crust. Determining the degassing rate of radiogenic ^{40}Ar through time is important for a number of geoscientific problems such as the growth regime of the continental crust, the potassium content of the silicate reservoirs, variations in mantle convection rate and global tectonics. Consequently, there have been several attempts to determine the rate of ^{40}Ar degassing from measurements of the Ar isotope composition of ancient atmosphere presumably preserved in sedimentary rocks and ice of known ages. The first unambiguous result was obtained for the Devonian Rhynie chert by (Cadogan 1977) and later confirmed by further analysis of the same unit by other groups. Cadogan (1977) measured a $^{40}Ar/^{36}Ar$ ratio of 293.0±1.6 (renormalized to the new value of the modern $^{40}Ar/^{36}Ar$ ratio of 298.6, Lee et al) for argon trapped in this 396 Ma-old chert. Assuming that this value represents the Ar isotope composition of air at that time and from its difference relative to the present-day $^{40}Ar/^{36}Ar$ value, it is straightforward to compute a ^{40}Ar flux from the solid Earth of 6 x 10^7 mol/yr for the last 400 Ma. It is interesting to compare this flux with that from the mantle. The flux of ^3He from the mantle was initially estimated at 1,000 mol/yr (Craig, Clark and Beg 1975) but has been scaled down to about 500 mol/yr by

(Bianchi, et al. 2010) . With a mantle ^{4}He/^{40}Ar ratio of 2±1 (Moreira, et al. 1998) and a mid-ocean ridge ^{3}He/^{4}He value of 8±1 Ra (Graham 2002) , one finds that the contemporaneous flux of ^{40}Ar from the mantle is within the range (1.2-8.6) x 10^7 mol/yr. The flux value obtained from the Rhynie chert is within this range, but the large uncertainty on these numbers prevents one to derive conclusions on the importance of other ^{40}Ar sources such as the continental crust. A more positive approach to these estimates is to consider that there is a surprisingly good match despite the fact that these flux values address drastically different periods of time.

Recently, a novel approach to quantify the flux of ^{40}Ar from the solid Earth to the atmosphere has been developed by Bender et al. (Bender, et al. 2008) using the record of air trapped in deep ice cores from Antarctica. Air trapped in ice is, however, gravitationally fractionated and direct measurements of ice-trapped noble gas isotope ratios are not representative of ancient atmospheric compositions. Additionally, the ice record extends to less than one Ma and the expected Ar isotope variations are much lower than the precision attained by most current noble gas mass spectrometers. In order to circumvent these problems, Bender et al. first developed high precision analysis of argon isotopes by adapting stable isotope mass spectrometry (dynamic mass spectrometry, i.e. with pumps open and a variable leak inlet) since the amount of sample was large by noble gas standards. They achieved an amazing precision of 0.024 ‰ (2 σ) on Ar isotope ratio measurements. Second, they made use of the fact that Ar has 3 isotopes and the ratio between two of them, ^{36}Ar and ^{38}Ar, can be safely assumed to be constant through time, at least during the last Ma, since they are not significantly produced or destroyed by nuclear reactions. Diffusion is a mass-dependent process and, in the case of Ar, can be corrected for by measuring the relative proportions of the 3 isotopes of argon trapped in ice and assuming a mass dependent law for isotopic fractionation. They found a rate of change of the Ar isotope ratio of air (^{40}Ar/^{38}Ar in their case) of 0.066±0.014 ‰/Ma, which yields a ^{40}Ar outgassing flux of 11±1 x 10^7 mol/yr, in fact not very different from Cadogan (1977)'s value of 6 x 10^7 mol/yr averaged over the last 400 Ma . Bender et al. concluded that their flux could be well accounted for by the sum of degassing fluxes from the mantle and the continental crust. Additionally, they proposed that their method provides a new way to date old ice, especially when other age records have been erased, although uncertainties are large (±180 Kyr).

Future Directions

The future of studying variations in atmospheric noble gas compositions relies on developing instrumentation in order to better measure the small differences involved and (particularly for addressing the temporal evolution of atmospheric noble gases) identifying suitable samples.

Considerable advances have been made in the last ten years and multicollector noble gas mass spectrometers are now commercially available. Although commercially available noble gas mass spectrometers are typically used in 'static' (pumps closed) mode, data from Mark et al (Mark, Stuart and de Podesta 2011) show that high precision noble gas isotope ratio measurements are possible on small gas quantities (of the order ±0.5 permil on the $^{40}Ar/^{36}Ar$ ratio with 2 x10^{-12} mol Ar). These mass spectrometers can be relatively easily adapted for 'dynamic' (pumps open) measurements, resulting in the precisions available using adapted stable isotope machines (of the order 0.05 permil for Ar (Bender, Barnett, Dreyfus, Jouzel and Porcelli 2008; Lee, Marti, Severinghaus, Kawamura, Yoo, Lee and Kim 2006; Valkiers, Vendelbo, Berglund and de Podesta 2010)). Dynamic mass spectrometery has the ability to improve precision relative to static mass spectrometers, at the cost of requiring much (10^3) larger samples and of inducing mass fractionation during inlet of the gas into the mass spectrometer. Large sample sizes are difficult to handle, particularly for He and Ne which are difficult to separate by distillation, instead requiring chemical purification of large volumes of air. Instrumental mass fractionation resulting from the inlet leak is furthermore a major problem for measurement of He isotopes in air, because, with only two isotopes, it is difficult to quantify the magnitude of this fractionation during analysis.

Identification of suitable archives for noble gas (particularly He) isotope analysis is critical in order to determine temporal changes in noble gas composiitons. For the present-day atmosphere, air sampled since 1976 at Cape Grim, Tasmania, under the auspices of the CSIRO, constitutes an archive of choice.

Suitable natural archives need to be able to preserve atmospheric noble gases without significant in situ production or destruction of isotopes, and without isotopic fractionation or, at least with the possibility of correcting for such fractionation with accuracy. Thus the nature of suitable archives depends on the targeted time interval. For the last couple of thousand years, only changes in the He isotopic composition are expected to be detectable with modern mass spectrometry systems. Helium has, however a high diffusivity in many of the materials of interest, including glass and organics. Greater predicted variations in $^3He/^4He$ are offset by higher precision of Ar isotope measurements and ability to correct for mass discrimination.

For the last millenium, some success has been achieved using industrial slags and porcelain, and there are certainly other possibilities such as for example manufactured metal tools, munitions, scientific instruments etc.

For variations over the last Myr the ice record has proven to be exploitable for Ar isotopes and although this may be possible also for He isotopes, this poses a considerably greater challenge as a) helium may diffuse through ice over these timescales; b) helium has only 2 isotopes and correction for significant isotope fractionation will be model-dependent and c) the low abundance of He in the atmosphere and atmosphere-equilibrated liquids require large sample sizes.

For the 10^8-10^9 yr time intervals, the sedimentary record seems to be the only way to get ancient air but in many cases the noble gas record is likely to have been altered by isotope exchange and in-situ production. So far only one sedimentary unit (the Devonian Rhynie chert) seems to have preserved an ancient atmospheric noble gas record. There is little doubt that other time capsules exist and should be investigated such as amber, evaporites, chert, and barite. Recently, Pujol et al (Pujol, et al. 2009) claimed that noble gases trapped in Archean barite were representative of the Archean atmosphere. in particular, they found that the stable isotope composition of xenon was intermediate between that of the modern atmosphere and that of primitive meteorites, suggesting time-dependent evolution for such composition.

With the advent of modern noble gas mass spectrometry and of novel analytical techniques, there is no doubt that we are opening a new chapter in the field of noble gas geochemistry with precise studies of the atmospheric evolution in space and time.

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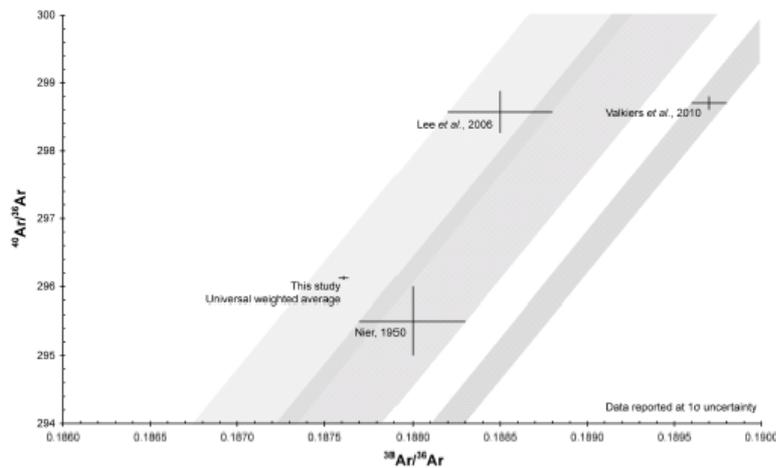
FIGURE 1: Estimates of atmospheric Ar isotope ratios (modified after Mark et al 2012). Lee et al (2006) and Valkiers et al (2008) refined the original Nier ^{40}Ar/^{36}Ar ratio but were unable to agree on an atmospheric ^{38}Ar/^{36}Ar value. Mark et al measured atmospheric Ar without constraining fractionation, therefore Mark et al's value (the value shown is the average of 180 measurements with the reported standard error) should fall all on the mass fractionation line passing through the true value. The slanted grey bars indicate the mass fractionation line (and associated uncertainty) passing through the three (Nier, Lee and Valkiers) absolute measurements. Mark et al's data are consistent with the Lee et al estimate of the atmospheric Ar.
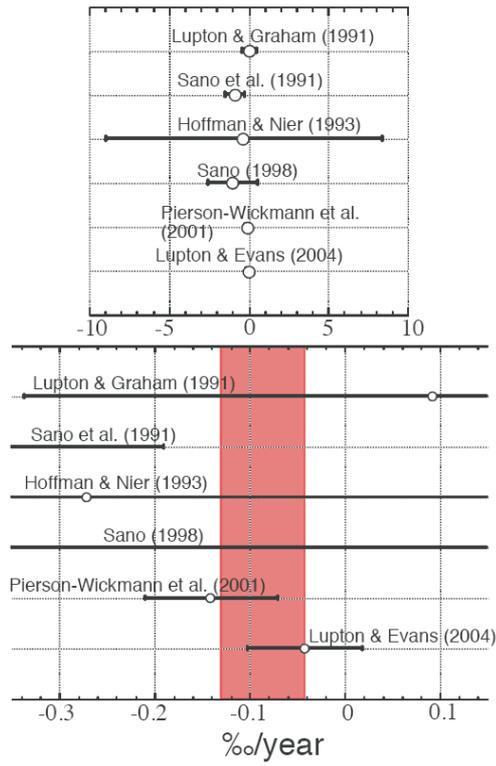
Figure 2.   A compilation of the time rate of atmospheric ^{3}He/^{4}He changes in the literature. Top and bottom show the change (‰/year) on large and small scales, respectively.
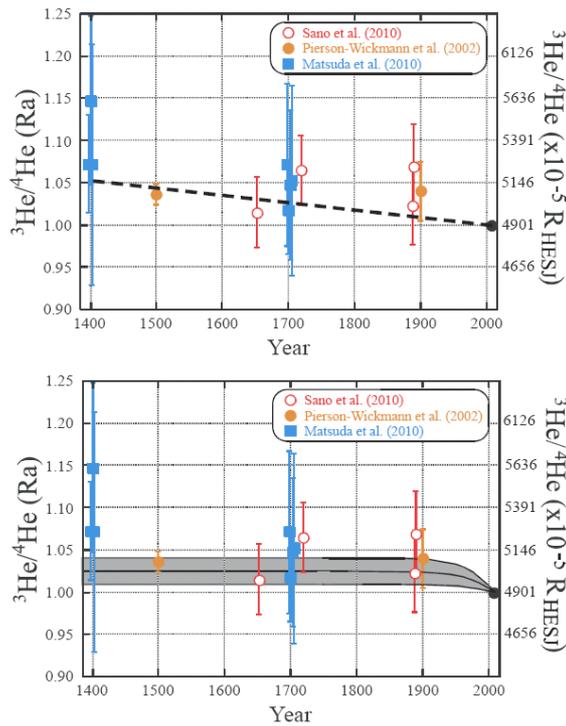
Figure 3. Secular variation of atmospheric ^{3}He/^{4}He ratio estimated from historical metallurgical slag and old Chinese porcelain. A dotted line in the top shows a simple linear regression taking into account of weighted errors. The curve in the bottom shows a simulation of the ^{3}He/^{4}He change based on fossil fuel consumption (see text). The gray area in the lower panel is obtained by the uncertainty of ±65% based on the He/C values of natural gas and petroleum.
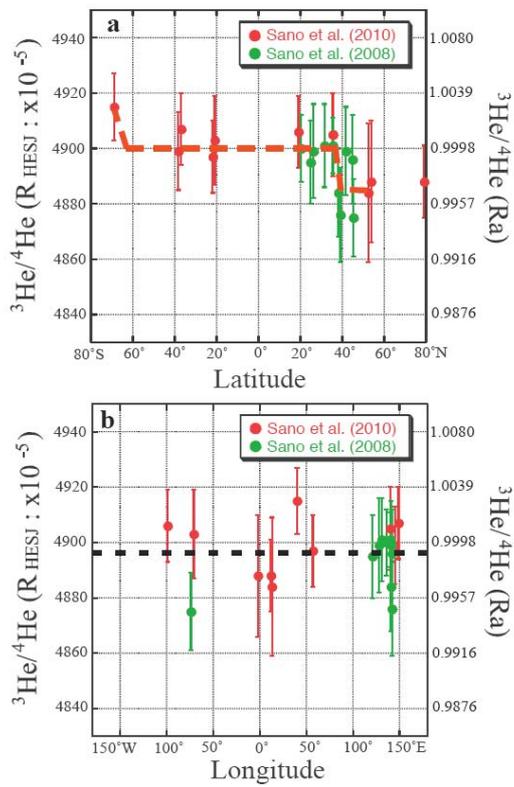
Figure 4. The changes of atmospheric ^{3}He/^{4}He ratio with latitude (a) and longitude (b). The ^{3}He/^{4}He ratios appear to increase from north to south but they are constant from east to west.