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# Increasing atmospheric helium due to fossil fuel exploitation

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Fossil fuels contain small amounts of helium which are co-released into the atmosphere together with carbon dioxide. However, a clear buildup of helium in the atmosphere has not previously been detected. Using a high-precision mass spectrometry technique to determine the atmospheric ratio of helium-4 to nitrogen, we show that helium-4 concentrations have increased significantly over the last five decades. Obtaining a direct measure of the rise in atmospheric helium-4 is possible because changes in nitrogen are negligible. Based on 46 air samples acquired between 1974 and 2020 we find that the helium-4 concentration increased at an average rate of 39±3 billion mol per year ($2\sigma$). Given that previous observations have shown that the ratio between helium-3 and helium-4 in the atmosphere has remained constant, our results also imply that the concentration of helium-3 is increasing. The inferred rise in atmospheric helium-3 greatly exceeds estimates of anthropogenic emissions from

**natural gas, nuclear weapons and nuclear power generation, suggesting poten-**

**tial problems with previous isotope measurements or an incorrect assessment**

**of known sources.**

# Main

Natural gas is enriched in $^4$He from radioactive decay of thorium and uranium in the Earth's crust. Anthropogenic fossil fuel usage has therefore greatly increased the release of crustal $^4$He to the atmosphere over the natural background rate [1–10]. In contrast, most natural gas sources are thought to be less enriched in $^3$He. The extraction of natural gas is thus expected to increase the $^4$He abundance of air while decreasing the $^3$He/$^4$He ratio [1–10].

$^3$He/$^4$He studies over the last four decades have yielded conflicting results, with early observational studies [1, 11, 12], studies based on air trapped in ceramics and metallurgical slags [6, 7, 13], and global helium budget calculations [2, 7, 10] supporting the existence of an anthropogenic signal whereas several independent measurements with improved error margins recently constrained any atmospheric $^3$He/$^4$He trend to be indistinguishable from zero [3, 4, 14, 15]. However, the precision of helium isotope measurements is currently limited to about 1 per mille per sample due to the low abundance of the rare isotope $^3$He in the atmosphere. Furthermore, other sources of $^3$He could partly offset the decline $^3$He/$^4$He from fossil-fuel extraction [4, 15].

Here we present high-precision measurements of $\delta(^4\text{He}/\text{N}_2)$ in archived air samples, which improve the ability to detect the $^4$He buildup by almost 2 orders of magnitude owing to the higher and more stable abundance of $\text{N}_2$ than $^3$He.

# Atmospheric $He/N_2$ rise

We analyzed 46 air samples collected at Scripps Institution of Oceanography (California, USA), Trinidad Head (California, USA), and Cape Grim (Australia) between 1974 and 2020. Samples were pumped either into high-pressure aluminum cylinders, chrome-molybdenum steel cylinders or 34L stainless steel "Essex tanks" (Essex Cryogenics, Missouri, USA) using different pumping systems (see methods). Samples were screened for leakage during storage and corrected for a small artifactual fractionation caused during sample collection (see methods). $^4He/N_2$ was measured using a novel mass spectrometric technique that relies on measuring $^4He$ in a continuous flow of air which has had all non-noble gases removed using a hot titanium getter. The method effectively determines relative differences in the helium mole fraction between sample and standard air, which are combined with information from separate measurements of $O_2/N_2$, $Ar/N_2$ and $CO_2$ to calculate $^4He/N_2$ [16]. Reporting the $^4He/N_2$ rather than the helium mole fraction directly is desirable because $N_2$ has remained stable in the atmosphere to within 0.01 per mille over the last decades while the overall composition of the atmosphere has changed [16]. Accounting for uncertainty in the fractionation correction and supplementary gas data, we estimate an overall analytical uncertainty of 0.07 per mil ($2\sigma$) for the $^4He/N_2$ measurement (see methods).

The results (Fig. 1) show that observed change in atmospheric $^4He/N_2$ between 1974 and 2020 is 1.93±0.14 per mille, corresponding to a average increase of 0.042±0.003 per mille per year ($2\sigma$ error from bootstrapping) or 39±3 billion mol of $^4He$ (atmospheric $^4He$ inventory: $9.268 \times 10^{14}$ mol). The $^4He$ buildup accelerates and reaches ~50–53 billion mol y$^{-1}$ between 2010 and 2014. This is two orders of magnitude greater than fluxes in the natural background state characterized by slow crustal degassing and He escape to space [8, 10, 17, 18] so must be anthropogenic in origin. The trend is generally lower than the estimated anthropogenic impact

in global inventories of $^4$He emissions [2, 7, 10].

The results also show shorter-term variability of uncertain origin. The spread of Essex tank data around a best-fit line is about two times larger than expected from the analytical uncertainty alone; the spread of data points from chrome-molybdenum steel cylinders is even higher, in particular before the year 2000. While the short-term variability in the Essex tanks could result from real atmospheric variability, the much greater variability in data from steel cylinders is almost certainly an artifact, which could be related to undocumented differences in the agent used to dry the air samples. For example, 13X molecular sieve was likely used for some steel cylinders before 2000 and laboratory tests suggests an associated risk of fractionation (Extended Data Fig. 2). Essex tanks in contrast were never subject to any chemical purification and thus provide a higher fidelity record. Despite the short-term variability, agreement between Essex tanks and high-pressure cylinders is good, and results from tank G-038 filled at Cape Grim in 1995 on a different pumping system agree with the observations from the Northern Hemisphere. This shows that our samples are unlikely to be affected by helium leakage and that we reliably capture a global signal.

If we assume that helium emissions are tied to natural gas emission, we can quantify the average helium content of natural gas globally. In Figure 1, we fit a trendline to the atmospheric $^4$He/N$_2$ history that is directly proportional to the cumulative global natural gas emissions from from (i) natural gas production, (ii) flaring, and (iii) fugitive fossil methane emissions (Extended Data Fig. 1). This fit, which largely explains the curvature, yields a constant scale factor that corresponds to a mean $^4$He content of 0.030±0.002% in natural gas (mol $^4$He per mol C). Our estimate of cumulative natural gas emissions presumably already accounts for a large fraction of helium release associated with oil and coal because helium will be primary found in the gas fraction, i.e. associated petroleum gas or coalbed methane. Also, Oliver et al.[2] showed that coal likely makes a negligible contribution to overall helium emissions due to its young age and

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insufficient uranium content.

Incidentally, the measured global $^4$He buildup vastly exceed [exceeds] the helium released from commercial use in manufacturing, research and medical equipment. Commercial helium production from 2010 to 2014 was between 5-8$\times 10^9$ mol y$^{-1}$ [4, 19], thus accounting for only 9–15% of the observed helium trend.

We are not aware of any other processes that significantly contributes [contribute] to the $^4$He/N$_2$ trend. Based on representative helium content of groundwater and anthropogenic usage, we estimate that the effect of human groundwater use on He/N$_2$ is very small. Helium concentrations in groundwater typically fall between $10^{-8}$ and $10^{-5}$ cm$^3$ (STP He) cm$^{-3}$(H$_2$O) depending on the age of the water and geological setting [e.g., 20–23]. Human groundwater usage was 952 km$^3$ y$^{-1}$ in 2010 [24] which places an upper limit on the degassing of helium from extracted groundwater of around 4.3$\times 10^8$ mol y$^{-1}$ or 0.46 per meg y$^{-1}$. The impact from natural degassing of fossil groundwater that has accumulated crustal He in regions previously frozen during the last glacial [period] is similarly negligible [5, 7]. Birner et al. [25] recently discussed a stratospheric influence on tropospheric $^4$He/N$_2$ via changing circulation. However, any such long-term variability is likely smaller than 0.5 per meg y$^{-1}$.

# Atmospheric $^3$He

In conjunction with previous studies of changes in atmospheric $^3$He/$^4$He, the observed $^4$He/N$_2$ trend puts [may put] important constraints on the release of $^3$He to the atmosphere (Fig. 2). We average three independent observation of the $^3$He/$^4$He trend [3, 4, 14], weighing them by variance, which yields a change of +8$\pm$20 per meg y$^{-1}$ (2$\sigma$). To simultaneously satisfy both observational constraints, a rise of $^3$He/N$_2$ by 49$\pm$20 per meg y$^{-1}$ is needed, which is equivalent to an additional release of about 63000$\pm$25000 mol $^3$He per year into the atmosphere (atmospheric

107   $^3$He inventory: $1.27\times10^9$ mol).

108     What could explain the $^3$He buildup implied by the $^4$He/N$_2$ and $^3$He/$^4$He measurements?

109 We briefly explore three different possibilities: (i) the observations ~~we~~ used to determine the

110 atmospheric $^3$He/$^4$He are incorrect, (ii) the $^3$He content of natural gas is greater than previously

111 thought, and (iii) there is an additional, unknown source of $^3$He.

112     In the absence of a significant $^3$He source, $^3$He/$^4$He should really be decreasing at a rate of

113 0.042±0.003 per mille per year. This seems improbable given that recent data from three inde-

114 pendent studies agree and show no significant helium isotope trend (Fig. 2). The three selected

115 studies represent the most recent, high-precision investigations of the helium isotope trend and

116 are based exclusively on samples stored in metal containers which addresses concerns about

117 previous observations regarding limited analytical precision [5], fractionation, helium leakage,

118 and *in-situ* helium production [e.g., 6, 7]. However, there is some contradictory evidence pub-

119 lished previously by other authors [e.g., 1, 6, 7, 12, 13] and we cannot completely rule out that

120 atmospheric helium isotope ratios are declining.

121     The $^3$He/$^4$He observations could be explained if natural gas really had a $^3$He/$^4$He ratio

122 1.18±0.49 greater than in the atmosphere. Such a high ratio can not be completely ruled out

123 as the $^3$He/$^4$He ratio of helium in natural gas is poorly known globally and can vary greatly

124 between different wells [e.g. 26–29]. The ratio depends on the presence of mantle-derived

125 primordial helium as well as the mineralogical composition of the gas' source region, i.e., the

126 relative abundance of lithium, uranium and thorium containing minerals which produce $^3$He

127 and $^4$He in decay reactions. Although the issue is not settled, published studies on He isotopes

128 have generally assumed a much lower ratio in fossil fuels [e.g., 1–6, 30], as expected from the

129 low average $^3$He/$^4$He ratio of 1.08E-08 in the Earth's upper crust [31].

130     The implied $^3$He increase constitutes a perturbation on top of the steady-state natural de-

131 gassing of $^3$He into the atmosphere which has been estimated to be an order of magnitude

smaller [8]. Known anthropogenic sources include production from tritium decay (half-life of 12.3 years) in the nuclear weapons stockpile, energy production and atmospheric weapons testing. These tritium sources alone, however, are insufficient to explain the observed helium trend and tritium release is heavily monitored. The continuous production from the nuclear stockpile and the historic input from nuclear weapons testing average over the last six decades to an annual input of roughly 2000–4000 mol $y^{-1}$, which is more than an order of magnitude smaller than the implied atmospheric $^3$He buildup [4]. To date, cumulative production of tritium in pressurized heavy water reactors has likely been less than the tritium added by atmospheric weapons testing [32].

Overall, this presents a major puzzle in the $^3$He budget which motivates a search for missing $^3$He sources on Earth, especially since $^3$He is considered an important, yet scarce resource [33].

# Summary and conclusions

Measurements of the $^4$He/$N_2$ ratio in 46 high-pressure samples of archived old air using a new mass spectrometric technique [25] reveal an atmospheric buildup of $^4$He of 0.042±0.003 per mille $y^{-1}$ ($2\sigma$), or 39±3 billion mol per year between 1974 and 2020. The atmospheric rise of $^4$He/$N_2$ accelerates from roughly 0.02 to 0.065 per mille $y^{-1}$ over the record, matching the exponential rise in fossil fuel exploitation. Assuming that helium release associated with natural gas emissions is the primary cause of the observed trend implies a mean helium content in natural gas of 0.030±0.002%, which is an order of magnitude less than commonly used estimates [2, 34]. A comparison of our results with previous observations of a near-zero trend in atmospheric $^3$He/$^4$He [3, 4, 14] suggests a so-far unidentified source of the scare resource $^3$He.

# Acknowledgments

# Author contributions

BB carried out the measurements and data analysis with support from BP, JS and RK. BB prepared the manuscript which was subsequently edited by all authors.

# Competing Interests statement

The authors declare to have no competing interests.

# Figures and Tables

Figure 1: Atmospheric $^4$He/N$_2$ change relative to the average of samples in 2020 CE. Data are shown from high-pressure chrome-molybdenum steel cylinders (grey circles), aluminum cylinders (gray diamonds), 34 L stainless steel Essex tank filled in the Northern Hemisphere (NH, black circles) and one Essex tank filled at Cape Grim in the Southern Hemisphere (SH, blue diamond) with $2\sigma$ error bars. Using independent observations of $\delta(\mathrm{Ar/N_2})$, grey data points were corrected for a small bias introduced during sampling (see methods). The best-fit line (red) is obtained by scaling global cumulative natural gas emissions (Extended Data Fig. 1) by a constant while maintaining the curvature of the emissions trend. The observed atmospheric buildup implies a mean helium content of 0.03±0.002% in natural gas assuming other fossil fuel contributions to the trend are negligible [2]. Uncertainty about the effective sampling date for mixtures of air from multiple days (see Extended Data Table 2) is smaller than the size of the data points.

Figure 2: Atmospheric $^3$He/$^4$He trend and inferred $^3$He emissions. The observed trend in atmospheric $^3$He/$^4$He is compared to a $^3$He/$^4$He trend calculated from our $^4$He/N$_2$ measurements assuming no $^3$He was being added to the atmosphere simultaneously. Dashed lines show the variance-weighted mean trends and error bars are $2\sigma$ uncertainties. The discrepancy between the measurements implies an atmospheric $^3$He buildup of 49±20 per meg y$^{-1}$.

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## Methods

### Delta values definition

We report changes in $^4\mathrm{He}/\mathrm{N}_2$ in delta notation:

$$\delta(^4\mathrm{He}/\mathrm{N}_2) = \frac{(^4\mathrm{He}/\mathrm{N}_2)_{\mathrm{SA}}}{(^4\mathrm{He}/\mathrm{N}_2)_{\mathrm{ST}}} - 1 \tag{1}$$

where subscripts SA and ST refer to the ratio in a sample and standard reference gas, respectively. $\delta(^4\mathrm{He}/\mathrm{N}_2)$ is either multiplied by $10^3$ and reported in "per mille" units or multiplied by $10^6$ and expressed in "per meg" units.

### Sampling

We analyzed the composition of clean ambient air pumped into pressurized containers by different laboratory groups at irregular times over the last five decades. The samples broadly fall into two groups: those collected in high-pressure cylinders made from aluminum or chrome-molybdenum steel (herein called "high-pressure cylinders"), and those collected in 34 L stainless steel "Essex tanks" (Essex Cryogenics, Missouri, USA). The properties of all samples used in this study are detailed in Extended Data Table 2.

#### Essex tanks

All but one Essex tanks were pumped as Advanced Global Atmospheric Gases Experiment (AGAGE) standards at either La Jolla or Trinidad Head on an oil-free compressors (RIX Industries, model SA-6B) up to 600–900 psi (4.1–6.2 Mpa) without any purification stage [35, 36]. Small amounts of deionized water were added during the filling processes to cool the pump. Essex tank G-038 was filled at Cape Grim using the cryogenic air sampling system described

in Brennwald et al. [5]. Essex tanks are sealed with all-metal valves connected to the tank body using metal-to-metal seals or elastomer-coated National Pipe Tapered (NPT) thread. Nine Essex tanks were excluded from this analysis because they exhibit a clear 2–5 per mille positive bias in the helium mole fraction compared to other tanks filled at similar times. For the excluded tanks, no corresponding anomaly is evident in $Ar/N_2$ or $O_2/N_2$, which suggests that these samples were contaminated with helium at the time of filling. Furthermore, Essex tanks with a remaining pressure below 1.5 MPa were not considered due to an apparent fractionation emerging only at very low pressures (SI).

**Aluminum and chrome-molybdenum steel cylinders**

All high-pressure cylinders were pumped at Scripps Institution of Oceanography (SIO) using a separate oil-free compressors (RIX Industries), with additional chemical processing specific to individual tanks. The processing variously included any of the following: passing through high-pressure columns containing Ascarite, $Mg(ClO_4)_2$, or 13X molecular sieve, Aquasorb® and additions of pure $CO_2$, $N_2$, and $O_2$. We expect these modifications to impact only select gases, with generally small or correctable impacts on $He/N_2$. The use of 13X molecular sieve was common in the earlier part of the record but no complete documentation of this is available in the lab notebooks. Air was also temporarily archived on occasion for later use, but was typically stored for no longer than a few weeks. Some cylinders contain a blend of air from up to 3 different sampling dates which was subsequently combined using a diaphragm gas transfer compressor (Compresseurs a membrane Corblin, type: A1C250). We only consider cylinders with multiple fill dates if they are less than a year apart and assign a representative fill date based on the contribution of each date to the overall cylinder composition. Many of the cylinders have been used to create Northern Hemisphere background records for perfluorocarbons $CF_4$, $C_2F_6$, and $C_3F_8$ [37]. We update the fill history of Mühle et al. [37] based on additional old logs and

302 lab notebooks. One high-pressure cylinder (LL9082) was filled with the same pumping system

303 used for the Essex tanks and demonstrates the comparability of the two filling systems. We

304 exclude Viton-sealed cylinders from our analysis due to known issues with permeation [38].


## Summary of analysis methods

306 Our measurements of $^4$He/N$_2$ are based on a new mass spectrometric analysis method described

307 in Birner et al.[16]. The measurement relies on stabilizing the flow of air to a mass spectrometer

308 (MS) to very high precision and monitoring changes in the $^4$He$^+$ beam while switching between

309 a sample and reference gas. Variability in the $^4$He$^+$ beam can thus be interpreted as a measure of

310 the difference in helium mole fraction between the sample and standard gas. The helium mole

311 fraction measurement can be combined with measured changes in O$_2$/N$_2$, Ar/N$_2$ and the CO$_2$

312 mole fraction to calculate the change in $^4$He/N$_2$ using the equation given by Birner et al.[16]:

$$\delta(\text{He/N}_2) \approx \delta(\text{He/M}) + \delta(\text{O}_2/\text{N}_2)\text{X}_{\text{O}_2} + \delta(\text{Ar/N}_2)\text{X}_{\text{Ar}} + \text{dX}_{\text{CO}_2} \tag{2}$$

313 where $\delta(\text{He/M})$ is the helium mole fraction expressed in delta notation following eq. 1 with

314 $\text{M} \equiv \text{N}_2 + \text{O}_2 + \text{Ar} + \text{CO}_2 + \cdots$. $\text{X}_{\text{O}_2}$ and $\text{X}_{\text{Ar}}$ are a representative values of the atmospheric

315 oxygen and argon mole fraction, and $\text{dX}_{\text{CO}_2}$ denotes the change in the CO$_2$ mole fraction.

316 Air is gettered before entry into the MS to remove all non-noble gases and effectively con-

317 centrate He by a factor of $\sim$100. Where available, repeat measurements of He/M were aver-

318 aged. All samples were measured against the same reference gas cylinder and He/N$_2$ data are

319 reported relative to the mean of all samples collected in 2020.

320 The reproducibility of repeat measurements of one standard cylinder over 8 months is 26 per

321 meg, but performance of the instrument was not uniform over the period of measurements (Ex-

322 tended Data Fig. 3). Before 25-May-2020 and following a careful calibration of the inlet

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system, a reproducibility of 10 per meg was achieved as reported by Birner et al.[16]. After 25-May-2020, a lower reproducibility of 29 per meg was obtained. The degradation followed several repairs to the analysis system including replacement of the sample and standard gas delivery lines to the flow-stabilizing inlet system, replacement of multiple MS electronic parts and the replacement of the entire MS source assembly, which required a recalibration of fractionation in the open split. As a conservative estimate, we use the reproducibility of 29 per meg after the repairs as a conservative estimate of $^4\text{He}/\text{N}_2$ measurement uncertainty. This precision is more than sufficient to resolve the expected per mille level changes in $\text{He}/\text{N}_2$ since the 1970s.

Measurements of $\text{O}_2/\text{N}_2$, $\text{Ar}/\text{N}_2$, and $\text{CO}_2$ in high-pressure cylinders were made using instrumentation and methods described by Keeling et al. [39, 40]. These data have a $1\sigma$ reproducibility of 2 per meg, 3 per meg and 0.03 ppm in $\text{O}_2/\text{N}_2$, $\text{Ar}/\text{N}_2$, and $\text{CO}_2$, respectively. $\text{CO}_2$ readings were taken from a Picarro G2401 analyzer for samples with $\text{CO}_2$ below 200 ppm due to concerns about the calibration validity of the primary instrumentation at such low $\text{CO}_2$ concentrations. Measurements of $\text{O}_2/\text{N}_2$, $\text{Ar}/\text{N}_2$, and $\text{CO}_2$ in Essex tanks were analyzed using the same method but using a second analysis system that included a separate a GV Isoprime mass spectrometer and a Licor Li-6251 $\text{CO}_2$ analyzer. The second instrument requires $\sim$10 times less gas for analysis, thus reducing sample usage. Repeatability of $\text{O}_2/\text{N}_2$, $\text{Ar}/\text{N}_2$, and $\text{CO}_2$ measurements on the second system was 2 per meg, 6 per meg, and 0.02 ppm ($1\sigma$), respectively. When applied in equation (2), these error yield a negligible combined uncertainty in correction from $^4\text{He}/\text{M}$ to $^4\text{He}/\text{N}_2$ of 0.4 per meg for both instruments due to the weighting by atmospheric abundance. The secondary mass spectrometer was calibrated with respect to the primary instrument by repeat measurements of a single standard.

## Helium leakage testing

The $He/N_2$ content of compressed air stored in high-pressure cylinders may potentially have decreased over time due to preferential permeation of He relative to $N_2$ through elastomeric seals, such as elastomeric valve seats and teflon tape on pipe threads for the head valves. To quantify the relevant He permeation rates, we exposed the cylinder head valves of several teflon-sealed and o-ring-sealed cylinders to 1–2 atmospheres of pure helium for 4–6 weeks. This process reverses and amplifies the partial pressure gradient of He between the environment and the cylinder, thus accelerating permeation. A leak sufficient to produce a 1 per meg drift in 1 year during storage, would yield a drift of roughly 10 per meg per day in the experiment. Cylinders were analyzed before and after exposure to the excess helium, allowing an additional month for the cylinder to rest after exposure before follow-on analysis. The drift rates in the experiment were scaled downwards by the ratio of the natural to amplified helium gradients to assess the expected actual drift rates of these tanks.

The permeation rates for select cylinders are summarized in Extended Data Table 1 and constrain equivalent $^4He/N_2$ loss rates in our samples to 3 per meg or less per year. This could lead to a drift of up to 120 per meg over 4 decades which is within the quoted uncertainty. Cylinder ND01645, in contrast, is suspected to have a compromised seal and produced a leak rate of 215 per meg per year, demonstrating the sensitivity of our test setup.

We expect the $He/N_2$ drift rates of the Essex tanks are comparable or smaller than that of the high-pressure cylinders. Essex tanks are sealed by all-metal valves connected to the tank body either via metal-to-metal Swagelok connections or Teflon tape seals on pipe threads. Our tests with high-pressure cylinders suggest that Teflon tape produces sufficiently tight seals to prevent problematic drift. Furthermore, we see no evidence in the time series for a dependence of $^4He/N_2$ on the seal type (see also Extended Data Fig. 4).

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## $^4$He/N$_2$ artifactual fractionation correction

We apply a small correction to $^4$He/N$_2$ data from high-pressure cylinders based on an apparent correlation with biases in Ar/N$_2$ compared to true atmospheric concentrations:

$$\delta(^4He/N_2) = \delta(^4He/N_2)_{raw} + (2.02 \pm 0.12) \times [\Delta(Ar/N_2) - \Delta(Ar/N_2)_{2020}] \qquad (3)$$

where $\delta(^4\text{He}/\text{N}_2)_{\text{raw}}$ are the uncorrected He/N$_2$ observations, $\Delta(\text{Ar}/\text{N}_2)$ is the Ar/N$_2$ anomaly, and $\Delta(\text{Ar}/\text{N}_2)_{2020}$ is the mean Ar/N$_2$ anomaly of cylinders in 2020. $\Delta(\text{Ar}/\text{N}_2)$ is defined as the difference between measured values in each cylinder and the true atmospheric value at the time of filling which was estimated based on extrapolating a fit to 15 years of flask data at La Jolla [40] (Extended Data Fig. 5). The correction coefficient is given by the slope of the best fit line [41] for the relationship between $\Delta(\text{Ar}/\text{N}_2)$ and the He/N$_2$ anomaly $\Delta(\text{He}/\text{N}_2)$ (Extended Data Fig. 2). In the absence of a known atmospheric history, $\Delta(\text{He}/\text{N}_2)$ is instead defined as the deviation of each sample from a second order polynomial fit to the uncorrected $^4$He/N$_2$ data (Extended Data Fig.5). For an Ar/N$_2$ anomaly of 200±6 per meg, the correction adds an uncertainty of 20 per meg ($1\sigma$) to our $^4$He/N$_2$ observation. Data from samples with $\Delta(\text{Ar}/\text{N}_2)$ exceeding 200 per meg are rejected. Essex tank data are uncorrected. A mechanism for the combined fractionation of Ar/N$_2$ and He/N$_2$ remains unclear. However, similarly correlated Ar/N$_2$ and He/N$_2$ anomalies were observed in an experiment in which cylinders were filled through a 13x molecular sieve, pointing to adsorption as a key process responsible for the artifactual fractionation. Adsorption is also consistent with a near 1:1 relationship observed between $\Delta(\text{Ar}/\text{N}_2)$ and $\Delta(\text{O}_2/\text{N}_2)$, where the O$_2$/N$_2$ anomaly $\Delta(\text{O}_2/\text{N}_2)$ is defined analogously to $\Delta(\text{Ar}/\text{N}_2)$, but further work would be needed to confirm the adsorption hypothesis.

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## Uncertainty propagation

We calculate an overall error of 35 per meg ($1\sigma$) for all samples by propagate uncertainty in quadrature from the initial $^4$He/M analysis, from the derivation of $^4$He/N$_2$, and from the artifactual fractionation correction (see Extended Data Table 3). This estimate is based on the worst-case scenario of a high-pressure cylinder with the maximum allowed artifactual Ar/N$_2$ fractionation of 200 per meg. Thus, it likely overestimates analytical uncertainty for Essex tanks slightly but allows us to use a consistent conservatively uncertainty value for all samples.

## Data availability

All data generated or analysed during this study are included in this published article as source data to Fig. 1 in the main text, Extended Data Figures 1–5 and Extended Data Tables 1–2.

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