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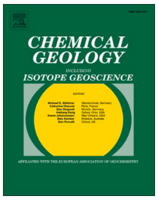

# Inter-laboratory re-determination of the atmospheric $^{22}Ne/^{20}Ne$

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## ABSTRACT

Accurate knowledge of the Ne isotopic composition of air is essential for planetary science. While the uncertainty of the noble gas isotopic composition of air has been drastically reduced to the level of ~0.1% in the last few years thanks to modern techniques, the most widely accepted value of the $^{22}Ne/^{20}Ne$ ratio of air (0.102 ± 0.0008, Eberhardt et al., 1965) has an uncertainty of ±0.78% (1σ). Here we present the first multi-laboratory re-determination of the atmospheric $^{22}Ne/^{20}Ne$. An artificial, high purity mixture of $^{20}Ne$ and $^{22}Ne$ was prepared and the $^{22}Ne/^{20}Ne$ (0.11888 ± 0.00001, 1σ) and $^{20}Ne/^{22}Ne$ (8.4118 ± 0.0007, 1σ) determined gravimetrically. This gas was used to determine the mass fractionation of five mass spectrometers allowing the air $^{22}Ne/^{20}Ne$ to be determined ($n = 234$ analyses). Each laboratory sampled their own local air, used a different gas preparation system and analysis procedure as well as doing their own expansion of the high-pressure artificial Ne gas. Individual air $^{22}Ne/^{20}Ne$ determinations have uncertainties in the range of 0.01–0.08%. The overall reproducibility of the calculated $^{22}Ne/^{20}Ne$ of air between the laboratories shows no overdispersion with respect to the individual uncertainties. We report a global value for the atmospheric $^{22}Ne/^{20}Ne$ of 0.10196 ± 0.00007 (0.07%, 1σ), equivalent of $^{20}Ne/^{22}Ne$ of 9.808 ± 0.007. This is almost identical to the Eberhardt et al. (1965) value although its uncertainty shows a 12 times reduction. Our study did not verify any of the other previous determinations of atmospheric $^{22}Ne/^{20}Ne$. This highly accurate and precise atmospheric $^{22}Ne/^{20}Ne$ value provides a new reference for atmospheric $^{21}Ne/^{20}Ne$ determinations and we recalculate $(^{21}Ne/^{20}Ne)_{air}$ of five recent determinations. While this exercise resulted in no significant change to the absolute values, it gives more confidence with respect to the correctness of $(^{21}Ne/^{20}Ne)_{air}$. We suggest that the revised value for atmospheric $^{22}Ne/^{20}Ne$ be used routinely in all geoscience applications.

## 1. Introduction

Accurate and precise determination of the isotopic composition of the noble gases in Earth's atmosphere is crucial for geosciences. Air is routinely used to determine the mass discrimination during isotope ratio measurements by noble gas mass spectrometers. Additionally, air-derived noble gases are present in all terrestrial mineral, rock and fluid samples to various degrees. Accurate determination of the isotopic composition of a sample requires a correction for the air contribution.

Neon isotopes are exceptional geochemical tracers due to the natural presence of three stable isotopes: $^{20}Ne$, $^{21}Ne$ and $^{22}Ne$. All of these isotopes are primordial and are produced by nuclear processes in the Earth, mostly via reactions of α - n from $^{17,18}O$ and $^{19}F$, $\beta^+$ from $^{22}Na$, α - p from $^{19}F$, n - α from $^{24,25}Mg$ and p - α from $^{23}Na$. Consequently, neon isotopes are used to determine the origin of terrestrial volatiles and the structure and degassing history of the Earth's interior and they are used as geochronometer (Colin et al., 2015; Moreira et al., 1998; Mukhopadhyay et al., 2012). Cosmogenic $^{21}Ne$, produced in minerals close to the surface by cosmic rays has been used to constrain the timescale of landscape evolution and glaciation processes (Codilean et al., 2008; Ritter et al., 2018). In extraterrestrial material cosmogenic neon is also used to unravel lunar surface processes and the space exposure history of

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meteorites (Füri et al., 2020; King et al., 2022; Nottingham et al., 2022; Wieler, 2002). The combination of primordial and nucleogenic sources of Ne make the isotope composition a useful U/Th – Ne geochronometer (Farley and Flowers, 2012; Farley and McKeon, 2015; Gautheron et al., 2006) and a powerful tracer of, for instance, fluids in the crust (Ballentine et al., 2005; Byrne et al., 2021; Gilfillan et al., 2019; Györe et al., 2021b). Another use of Ne isotopes is for example to improve volcanic eruption forecasting (Alvarez-Valero et al., 2022).

Developments of noble gas mass spectrometry in the last two decades have seen a significant improvement in the repeatability of He, Ne and Ar isotopic ratio measurements (Farley et al., 2020; Györe et al., 2021a; Mark et al., 2011; Marrocchi et al., 2009; Mishima et al., 2018). This led to the precise redetermination of, for instance, $^{21}$Ne/$^{20}$Ne of air (Györe et al., 2019; Honda et al., 2015; Mark et al., 2011; Saxton, 2020; Wielandt and Storey, 2019). The precision of $^{21}$Ne/$^{20}$Ne, typically 0.1%, relies on a reference value of $^{22}$Ne/$^{20}$Ne.

Previous determinations of the $^{22}$Ne/$^{20}$Ne value of air vary between 0.10186 ± 0.00032 (Walton and Cameron, 1966, single collector Faraday) and 0.102370 ± 0.000012 (Valkiers et al., 1994, MAT 271 mass spectrometer). The most widely used $^{22}$Ne/$^{20}$Ne value is that of Eberhardt et al. (1965) (single collector Faraday) (0.1020 ± 0.0008) (0.78% uncertainty, 1σ). This was obtained by combining gravimetry and mass spectrometric analysis, the latter providing the most significant source of uncertainty. Although Valkiers et al. (2008) obtained a much more precise value (0.101975 ± 0.000002), it is not widely used because it was obtained from raw ion current ratios only.

Gravimetry is routinely used to determine gas concentrations because mass can be obtained with a low uncertainty (Yang et al., 2017). The application of gravimetric noble gas 'standards' includes the determination of the atmospheric $^{40}$Ar/$^{36}$Ar (Lee et al., 2006) and $^{22}$Ne/$^{20}$Ne (Bottomley et al., 1984; Eberhardt et al., 1965). Such standards have been used to determine the Boltzmann constant (de Podesta et al., 2013; Fellmuth et al., 2006; Valkiers et al., 2010), the Avogadro constant (Valkiers et al., 1998) and the triple point of Ne as well as to calibrate cryogenic thermometry (Hill and Fahr, 2011; Pan et al., 2021; Pavese et al., 2013; Steur et al., 2013; Steur et al., 2015; Steur et al., 2019).

Here we use a high purity gas mixture of $^{22}$Ne and $^{20}$Ne that was prepared gravimetrically to determine the isotopic fractionation intrinsic in state-of-the-art noble gas mass spectrometers to produce an order of magnitude reduction of the uncertainty of the air $^{22}$Ne/$^{20}$Ne. This is a multi-laboratory exercise based on a high number of mass spectrometric measurements. We use the new $^{22}$Ne/$^{20}$Ne to recalculate the atmospheric $^{21}$Ne/$^{20}$Ne of air.

## 2. Analytical procedure

### 2.1. The artificial $^{22}$Ne – $^{20}$Ne gas mixture

#### 2.1.1. Preparation

Gravimetric preparation of Ne standards was undertaken at Korea Research Institute of Standards and Science (KRISS) following established procedures (Lee et al., 2006; Steur et al., 2013; Yang et al., 2017). Chemically and isotopically pure $^{20}$Ne was obtained from ICON Isotopes (USA) with nominal chemical and isotopic purity better than 99.999% and 99.99% respectively. Pure $^{22}$Ne was obtained from Linde with 99.9% chemical and isotopic purity.

The chemical and the isotopic purity were determined by a Finnigan MAT 271 mass spectrometer in the KRISS laboratory. To identify the impurities, a scan between mass 1–128 was conducted and only $H_2$, He, $CO_2$, $N_2$ and $O_2$ turned out to be higher than background. The sensitivity of these masses was pre-calibrated using standard gases KRISS owns and concentrations of the impurities were determined (Table 1). For isotopic impurity, the ion current ratio $r$($^{22}$Ne/$^{20}$Ne) of the sample introduced into the mass spectrometer was measured (Eq. (1)), where '$I$' is the ion current at a specific mass number measured by the mass spectrometer. Then, the ion current ratio was corrected by the small mass discrimination factor ($f_{MD}$) for the mass spectrometer at the given mass (Eq. (2)) to obtain the true ratio 'R'.

**Table 1**
Results of chemical and isotopic impurity analysis of $^{20}$Ne and $^{22}$Ne gases obtained for this study.

| Gas | $^{20}$Ne supplied by Icon | $^{22}$Ne supplied by Linde |
|---|---|---|
| | Concentration (μmol/mol) | |
| $^{20}$Ne | *999,937.3 (22.1)* | 1080.0 (11.1) |
| $^{22}$Ne | 19.0 (0.2) | *997,255.3 (34.9)* |
| $^{21}$Ne | 22.0 (0.2) | 1658.0 (17.1) |
| $H_2$ | 1.9 (1.9) | 6.5 (6.5) |
| He | 8.6 (8.6) | BDL |
| $CO_2$ | 6.9 (6.9) | BDL |
| $N_2$ | 4.2 (4.2) | BDL |
| $O_2$ | 0.1 (0.1) | 0.2 (0.2) |
| Elemental purity | 99.9978% | 99.9993% |
| Total | 1,000,000 | 1,000,000 |

Numbers in *Italic* indicate the isotope purity of the gas.
Elemental purity reflects the total concentration of components other than Ne.
Total values indicate no unknown contamination up to the level of 0.1 ppm (molar).
Uncertainties of the chemical impurity are taken as the impurity values itself (100% error).
Uncertainties on minor isotope impurity is taken as the mass discrimination factor (1.03%, see text).
Uncertainties on major isotope content is the sum of chemical and isotope impurity.
BDL: Below Detection Limit.

No unknown contaminant was measured at >0.1 ppm (molar) level in both gases, implying that they exceeded their nominal elemental purity (Table 1). The isotope purity of the $^{20}$Ne is 99.9937%, which is slightly higher than the nominal value (99.99%). The isotope purity of the $^{22}$Ne is only 99.7255%, slightly below the nominal value of 99.9%. The most significant contaminant of the $^{22}$Ne gas is $^{21}$Ne (1658 ppm), followed by $^{20}$Ne (1080 ppm) (Table 1).

$$r\left(\frac{^{22}\mathrm{Ne}}{^{20}\mathrm{Ne}}\right) = \frac{I\left(^{22}\mathrm{Ne}\right)}{I\left(^{20}\mathrm{Ne}\right)} \tag{1}$$

$$\mathrm{R}\left(\frac{^{22}\mathrm{Ne}}{^{20}\mathrm{Ne}}\right) = f_{\mathrm{MD}} \bullet r\left(\frac{^{22}\mathrm{Ne}}{^{20}\mathrm{Ne}}\right) \tag{2}$$

Three gas mixtures with different $^{22}$Ne/$^{20}$Ne ratios were prepared using gravimetric methods. The nominal $^{22}$Ne target concentrations in three $^{22}$Ne – $^{20}$Ne mixes were 9.5%, 10.5% and 12%. The procedure followed the same approach and procedure described in Steur et al. (2013), in which $^{22}$Ne target concentrations were 6.6%, 10% and 20%.

For gravimetric measurements, a high precision electronic mass comparator, Mettler Toledo model AX1005, equipped with an automated cylinder loading, was used. The instrument compares the mass of two objects with a maximum difference of 1.1 kg and minimum difference of 0.01 mg (9 ppb). Consequently, to determine the mass of a gas two identical cylinders (sample and tare cylinders) are required (Fig. 1).

Gas mixtures of $^{20}$Ne and $^{22}$Ne were prepared using a purpose-built stainless steel vacuum system, pumped to high vacuum, following the procedure suggested by the relevant international standard (ISO 6142-1, 2015) and works published previously (Lee et al., 2006; Yang et al., 2017) (Fig. 1). First, the sample cylinder (75 cm$^3$, Swagelok all-metal valve) was weighed against the tare cylinder. Then the sample cylinder was connected to the system and $^{22}$Ne was charged into it while pressure was recorded in the pressure gauge (~3 bar). The mass was measured relative to the tare cylinder producing the mass of the $^{22}$Ne in the cylinder. The sample cylinder was then connected again to the filling system and the system was filled with $^{20}$Ne and pressure recorded (~ 70 bar). Then $^{20}$Ne was added to the sample by opening the inlet valve of the cylinder until the pressure in the pressure gauge dropped to the

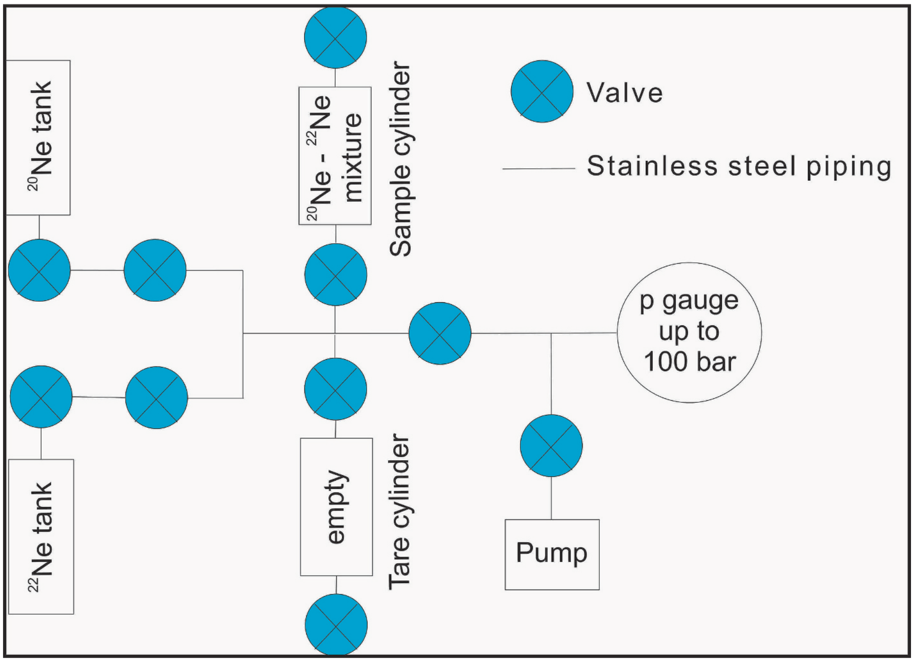

**Fig. 1.** Schematics of the apparatus used to prepare the artificial gas mixture of $^{22}$Ne and $^{20}$Ne at KRISS. At each step of the fill (empty, $^{22}$Ne charge and $^{20}$Ne charge), the mass of the sample cylinder was compared to that of tare cylinder using a Mettler Toledo model AX1005 precision electronic mass comparator.

**Table 2**
Gravimetric results of the gas mixture of $^{22}$Ne – $^{20}$Ne with nominal $^{22}$Ne content of 10.5%, prepared for this study.

| | Gravimetric measurements | | | |
|---|---|---|---|---|
| | Set 1 (g) | Set 2 (g) | Set 3 (g) | AVG (g) |
| Empty ($m_1$) | −0.43762 | −0.43760 | −0.43760 | −0.43761 (1) |
| After 1st fill ($^{22}$Ne), 3.37 bar ($m_2$) | −0.21133 | −0.21131 | −0.21132 | −0.21132 (1) |
| After 2nd fill ($^{22}$Ne – $^{20}$Ne), 33 bar ($m_3$) | 1.51483 | 1.51482 | 1.51482 | 1.51483 (1) |
| $^{22}$Ne content (g), (no impurity corr.) | 0.22629 | 0.22629 | 0.22628 | 0.22629 (2) |
| $^{20}$Ne content (g) (no impurity corr.) | 1.72616 | 1.72613 | 1.72614 | 1.72615 (2) |

Masses have been obtained from a mass comparator (see text). Negative masses are technical terms only and are relative to tare.
Each set of data shows the mean of 10 mass measurements. Error of mass measurements is 0.02 mg (see text).
1σ uncertainties as last significant figures are in parenthesis.

value pre-determined by the nominal ratios (~33 bar). Because the pressure in the filling line was at least twice as high as in the sample cylinder, the flow during this second fill was dominantly towards the sample cylinder and no loss of $^{22}$Ne occurred (Holland and Bragg, 1995). The mass measurement was repeated, yielding the total mass of Ne ($^{22}$Ne and $^{20}$Ne) in the cylinder. To achieve homogeneity, cylinders were turned over after each weighing. During the preparation, the sample cylinder with nominal target $^{22}$Ne concentration of 9.5% turned out to be leaking at the early stages and its preparation was stopped. Gas cylinders were left intact to allow homogenization for over a year.

The gas mixtures from both remaining cylinders were analysed on the Finnigan MAT 271 mass spectrometer at KRISS for verification (Steur et al., 2013). This step checks the internal consistency of the preparation of gas mixtures and compares it to other similar preparations (Steur et al., 2013). The verification process suggested that while the gas prepared with the nominal content of 10.5% $^{22}$Ne is consistent with the three mixtures published by Steur et al. (2013), the 12% $^{22}$Ne is not. This implies that during the preparation of the 12% $^{22}$Ne cylinder, a leak must have occurred. As a result, we only use the gas mixture with a nominal content of 10.5% $^{22}$Ne in this study. Gravimetric measurements are reported in Table 2.

#### 2.1.2. *Final $^{22}$Ne/$^{20}$Ne value of the Ne gas mixture and propagation of uncertainty*

Using gravimetric measurements, the chemical and isotope impurity of gases and molar masses of isotopes (Table 1 & 2), we calculate the $^{22}$Ne/$^{20}$Ne molar composition of our artificial Ne mixture to be 0.11888 using Eq. (3). For detailed steps, we refer the reader to Table 3.

$$\left(\frac{^{22}\mathrm{Ne}}{^{20}\mathrm{Ne}}\right) = \frac{\dfrac{\dfrac{x_{22_{Ne}} M_{22_{Ne}} (m_2 - m_1)}{\sum_{i=1}^{n} x_i M_i} + \dfrac{y_{22_{Ne}} M_{22_{Ne}} (m_3 - m_2)}{\sum_{i=1}^{n} y_i M_i}}{M_{22_{Ne}}}}{\dfrac{\dfrac{y_{20_{Ne}} M_{20_{Ne}} (m_3 - m_2)}{\sum_{i=1}^{n} y_i M_i} + \dfrac{x_{20_{Ne}} M_{20_{Ne}} (m_2 - m_1)}{\sum_{i=1}^{n} x_i M_i}}{M_{20_{Ne}}}} \tag{3}$$

In Eq. (3). $M_i$ is the molar mass of component i, $y_i$ and $x_i$ are the molar fraction of these components in $^{20}$Ne and $^{22}$Ne source gases, respectively (Table 1 & 3), $m_1, m_2$ $m_3$ refer to the sample cylinder mass as empty, after first fill ($^{22}$Ne) and after 2nd fill ($^{22}$Ne and $^{20}$Ne), respectively (Table 2).

The variance of the Ne isotope ratio can be calculated by summing the variance of all components, each of which can be obtained by the partial differentiation of Eq. (3). But before that, we will assess below what simplifications we can make. The uncertainty of the final ratio is determined by the concentration (mass) of the minor component. The

**Table 3**
Impurity correction for gas mixture of $^{22}Ne$ – $^{20}Ne$ with nominal $^{22}Ne$ content of 10.5%, prepared for this study and its final $^{22}Ne/^{20}Ne$ ratio.

| Component | Molar mass (g/mol) | Component mass in 1 mol $^{20}Ne$ source gas (g) | Actual component mass in $^{20}Ne$ source gas (g) | Component mass in 1 mol $^{22}Ne$ source gas (g) | Actual component mass in $^{22}Ne$ source gas (g) | Total mass (g) | Total amount (mol) |
|---|---|---|---|---|---|---|---|
| $^{20}Ne$ | 19.99244 | 19.9911 (4) | 1.72603 (6) | 0.0216 (2) | 0.000222 (2) | 1.72626 (6) | 0.086345 (3) |
| $^{22}Ne$ | 21.99139 | 0.000418 (4) | 0.0000361 (4) | 21.9310 (8) | 0.22571 (2) | 0.22575 (2) | 0.010265 (1) |
| $^{21}Ne$ | 20.99385 | 0.000462 (4) | 0.0000399 (4) | 0.0348 (4) | 0.000358 (4) | – | |
| $H_2$ | 2.01568 | 0.000004 (4) | 0.0000003 (3) | 0.00001 (1) | 0.0000001 (1) | – | |
| He | 4.00260 | 0.00003 (3) | 0.000003 (3) | – | – | – | |
| $CO_2$ | 43.98983 | 0.0003 (3) | 0.00003 (3) | – | – | – | |
| $N_2$ | 28.00614 | 0.0001 (1) | 0.00001 (1) | – | – | – | |
| $O_2$ | 31.98983 | 0.000003 (3) | 0.0000003 (3) | 0.000006 (6) | 0.0000001 (1) | – | |
| Total | – | 19.9925 (6) | 1.726150 (7) | 21.9874 (9) | 0.22629 (2) | – | 0.096611 (3) |
| | | | | | | | |
| Final values | | | | | | | |
| $^{22}Ne$ (%) | – | – | – | – | – | – | *10.625 (2)* |
| $^{22}Ne/^{20}Ne$ | – | – | – | – | – | – | *0.11888 (1)* |

*Italics*: Final values for the KRISS Ne gas of this study.
1σ uncertainties as last significant figures are in parenthesis.
Molar masses are after Audi and Wapstra (1993, 1995).
Impurity corrections are based on data from Tables 1 and 2.

minor component in the study of Lee et al., 2006 was 0.3% $^{36}Ar$ in pure Ar and the minor component in the study of Yang et al., 2017 was <0.1% Ar in an Ar - $O_2$ mixture. Thus, a rigorous and complex error propagation was necessary in those works. In contrast, the concentration of the minor component in this work is 10.625% (~0.22 g $^{22}Ne$). Thus, the complexity of the error propagation is much closer to that of Steur et al. (2013), where the concentration of the minor component ($^{22}Ne$) was 6.6%. This suggests that the impurity of the source gas (elemental and isotopic) (Table 1) and the repeatability of the weighing (Table 2) are the only factors to consider for the final uncertainty. Uncertainties originating from the molar masses are negligible and we can assume that mass measurements were independent of each other because of the single dominant isotope in each source gas. As a result, uncertainty propagation can be best described by Eq. (4).

$$\sigma^2\left(\frac{^{22}Ne}{^{20}Ne}\right) = \sum_{i=1}^{3}\left(\sigma_{m_i}\frac{\partial A}{\partial_{m_i}}\right)^2 + \sum_{i=1}^{2}\left(\sigma_{iso\ pur_i}\frac{\partial A}{\partial_{iso.pur.i}}\right)^2 + \sum_{i=1}^{2} \times \sum_{j=2}^{1}\left(\sigma_{iso_i in\ iso_j}\frac{\partial A}{\partial_{iso.i\ in\ iso.j}}\right)^2 \tag{4}$$

Where 'A' refers to Eq. (3), ∂ is the symbol for partial derivative and σ is the error on the mass measurement. The left side of the equation is the variance of the molar ratio of the two isotopes. The first term of the right side of Eq. (4) is the variance originating from the mass measurements ($m_1$, $m_2$, $m_3$ in Eq. (3)), which is a rather straightforward calculation. The second term is the variance originating from the purity for isotope 'i' ($^{22}Ne$ and $^{20}Ne$), including elemental purity and $^{21}Ne$. The third term is the variance originating from the minor component (either $^{22}Ne$ in $^{20}Ne$ or $^{20}Ne$ in $^{22}Ne$, 'i' or 'j') with the major isotope. Each term of the equation is discussed below.

The uncertainty of the mass measurements is 0.02 mg. This originates from the difference measured between tare and sample cylinders (see above). Rather than propagating this error, which would be very small due to the relatively large number of measurements (three sets, each being the mean of 10 mass measurements) we conservatively take the error on the mean of the three sets. This results in 0.015 mg and 0.02 mg error on the mass of $^{22}Ne$ and $^{20}Ne$ respectively. This demonstrates that the more significant source of error (0.068‰) is associated with the content of $^{22}Ne$ (minor component) as opposed to the error of the mass of $^{20}Ne$ (0.012‰).

The second item of the right side of Eq. (4) is derived from the chemical impurities and $^{21}Ne$ contamination of the gases. The uncertainty in chemical impurities is taken as the impurity values themselves (100% relative error). These are 21.7 ppm and 6.7 ppm for $^{20}Ne$ and $^{22}Ne$ source gases, respectively (Table 1). Our isotope impurity measurements in theory rely on mass spectrometric analysis. The mass discrimination factor of the MAT 271 at KRISS has been determined to be 1.03%. However, because both source gases used in this study have a single dominant isotope (either $^{20}Ne$ or $^{22}Ne$), the effect of the discrimination factor is negligible although it is accounted for. If we take the mass discrimination factor of 1.03% as the error itself (100% error), which is a large overestimation, we calculate the sum of elemental and $^{21}Ne$ isotope impurities to be 23.8 ppm and 21.9 ppm for $^{22}Ne$ and $^{20}Ne$ source gas, respectively.

The last item of Eq. (4) consists of the impurity of one of the isotopes of interest. The error on the contaminating isotopes is based on the mass discrimination factor and is calculated to be 17.1 ppm and 0.2 ppm for $^{22}Ne$ and $^{20}Ne$ source gas, respectively.

The verification process (Section 2.1.1.) carries no significance with respect to the overall uncertainty of the isotope ratio as per the relevant international standard (ISO 6142-1, 2015) and previous works (e.g. Lee et al., 2006; Steur et al., 2013). We calculate the final uncertainty of our artificial Ne gas mixture to be 0.01%, resulting in a final value for $^{22}Ne/^{20}Ne$ of 0.11888 ± 0.00001 and $^{20}Ne/^{22}Ne$ of 8.4118 ± 0.0007 (1σ).

### 2.2. Mass spectrometric analysis of the artificial Ne gas and air

Four laboratories undertook mass spectrometric measurements in order to re-determine the $^{22}Ne/^{20}Ne$ of air. Each laboratory determined the mass discrimination factor of the mass spectrometers via the analysis of the $^{22}Ne/^{20}Ne$ ratio of the artificial Ne gas (referred to as KRISS Ne gas). The mass discrimination value was then used to determine the $^{22}Ne/^{20}Ne$ of air based on repeated analysis of local air.

Each laboratory obtained a split of the same initial KRISS Ne gas mixture at the nominal pressure of 2 bar in 25 $cm^3$ vessels that were baked at ~373 K for 24 h and pumped down to below $10^{-9}$ mbar prior to gas fill. Rather than developing a common procedure, all laboratories developed their own analytical approach. This includes the expansion of the high-pressure gas into a volume from where gas aliquots were taken for mass spectrometric analysis, the fill of the air reservoir, the gas preparation and the analytical procedures. In this way the cross-laboratory exercise captured the diversity of techniques. Containers for each laboratory were filled at KRISS independently over a 6-month period. All laboratories used mass spectrometers, whose resolution is lower than necessary to fully separate isobaric interferences (Honda et al., 2015). The analytical procedure of each laboratory is described below.

### 2.2.1. ATOMKI

A 2 L reservoir was filled with Debrecen air (47°32′37.3" N, 21°37′25.1″ E) to 157 mbar. An aliquot of 0.125 $cm^3$ of air yields 1.02 × $10^{-10}$ mol $^{20}$Ne (2.29 × $10^{-6}$ $cm^3$ STP) which was used for analysis. The KRISS Ne gas was used to fill a 6-L reservoir at 3.57 mbar. The 2 $cm^3$ pipette delivered approximately the same Ne content as the air aliquot. For the KRISS Ne gas 2, 3, 5 and 8 aliquots of gas and for the corresponding air 2, 3, 4 and 7 aliquots of gas were analysed. This was done to avoid pressure effect. Both the air and the KRISS Ne aliquots were expanded to a stainless-steel empty trap held at 25 K to trap trace active gases ($O_2$, $N_2$, $CO_2$, $H_2$) and heavy noble gases (Ar, Kr, Xe). Then the He and Ne were adsorbed on a charcoal trap at 10 K operated by a cryogenic cooling system (Leybold). The charcoal trap was then heated to 43 K, and the trace He fraction was pumped for 1 min. The trap was then heated to 90 K and the neon fraction was admitted to two different mass spectrometers, a VG5400 and an MM5400 for Ne isotope ratio determinations in two separate experiments (Palcsu et al., 2014; Papp et al., 2012). While physically the two mass spectrometers are identical (resolution 150), they differ in their control software. The VG5400 is controlled by an in-house developed Noble Gas Software that has been developed using a Qt cross-platform application and UI framework under General Public Licence. The MM5400 control software has been written in LabView that runs under Windows. Both Ne peaks were measured by a single Faraday collector in peak jumping mode. All isobaric interferences were negligible (e.g. below 0.1‰). The KRISS Ne gas and air were measured in alternating cycles.

### 2.2.2. SUERC

The first KRISS Ne gas was received in April 2021. It was expanded into a ~ 2 L reservoir, from where a 0.2 $cm^3$ gas aliquot was expanded into another ~2 L reservoir, resulting in nominal delivery of 2.69 × $10^{-12}$ mol $^{20}$Ne/aliquot (6.02 × $10^{-8}$ $cm^3$ STP). The first air bottle of SUERC used in this study was filled by East Kilbride air (55°45′12.1" N, 4°09′43.1" W) in July 2017 to the level of 7.46 × $10^{-13}$ mol $^{20}$Ne/aliquot (1.67 × $10^{-8}$ $cm^3$ STP) and has been used for a number of studies as a calibration material (Gilfillan et al., 2019; Györe et al., 2021a; Györe et al., 2019). A second cylinder of the KRISS Ne gas was expanded in the same way 6 months later, in October 2021. A second bottle of air was filled at the same time at the pressure identical to the first one.

Aliquots of air were taken to a gas preparation system described earlier (Györe et al., 2019). The gas was purified by a SAES GP50 ZrAl alloy getter and heavy noble gases (Ar, Kr, Xe) were trapped by a charcoal finger at the temperature of liquid nitrogen (77 K) for 10 min. The remaining gas was exposed to a Sumitomo cold head (IceOxford) kept at 30 K for 15 min after which He was pumped, the Ne released at 78 K and admitted to the mass spectrometer for analysis. The analysis of the KRISS Ne gas followed the same procedure as that of air.

A Thermo Fisher ARGUS VI noble gas mass spectrometer (resolution of 200) was used for the analysis using $10^{12}$ Ω resistance Faraday amplifiers located at H2 and L2 positions for the simultaneous collection of $^{22}$Ne and $^{20}$Ne (Gilfillan et al., 2019; Györe et al., 2021a; Györe et al., 2019). Measurements were carried out at multiple aliquots of gases, at which level all isobaric interferences were <0.2‰. The analytical period lasted 6 months in a fully automated mode that required minimal human input twice a week. The $^{40}Ar^{2+}$ and $^{44}CO_2^{2+}$ interferences were kept as low as possible by a liquid nitrogen cooled cold charcoal trap located close to the ion source. Blank checks followed every second analysis of air and the KRISS gas. Mass discrimination factor was determined in two batches using the two KRISS Ne gases, followed by batch of analysis of air at different pressure levels bracketing that of the KRISS Ne gas to capture the potential effect of pressure on isotope ratios.

### 2.2.3. UC Davis

$^{20}$Ne amounts between 1.34 × $10^{-14}$ mol (3.00 × $10^{-10}$ $cm^3$ STP) and 2.98 × $10^{-14}$ mol (6.68 × $10^{-10}$ $cm^3$ STP) were measured from the air tank (Williams and Mukhopadhyay, 2019) to monitor pressure dependent effects. A shot of the KRISS Ne standard delivers 3.13 × $10^{-12}$ mol of $^{20}$Ne (7.01 × $10^{-8}$ $cm^3$ STP). Stepwise pressure reduction resulted in analyzing 2.58 × $10^{-14}$ mol of $^{20}$Ne (5.78 × $10^{-10}$ $cm^3$ STP), corresponding to 0.82% of the original aliquot. The procedure allowed the partial pressure of Ne from the KRISS standard in the mass spectrometer to be close to that of the air aliquots to reduce potential pressure dependent effects on mass discrimination.

The gases were sequentially exposed to a hot and cold SAES NP10 getter. Neon was then frozen onto a charcoal containing cryogenic trap at 32 K, a temperature at which He is not trapped. After He was pumped out, the cryogenic trap was warmed to 74 K to release Ne, which was let into a Nu Noblesse HR multi-collector instrument fitted with two Faraday cups and six ETP electron multipliers. Neon isotopes were measured simultaneously on electron multipliers. The mass resolving power (MRP) of the low mass collector used for measuring $^{20}Ne^{+}$ was 6800 (Saxton, 2020), which was sufficient to measure $^{20}Ne^{+}$ free from $^{40}Ar^{2+}$ interference. Average (HF + $H_2O$)/$^{20}Ne^{+}$ ratio was 3.9 × $10^{-5}$. The high mass collector used for $^{22}Ne^{+}$ had a MRP of 4500, which was not sufficient for resolving $^{44}CO_2^{2+}$ from $^{22}Ne^{+}$ and $CO_2^{+}$ beams were monitored during the Ne measurements to correct for the interference on $^{22}$Ne. $^{44}CO_2^{+}$ count rates were ~ 200 cps and the $^{44}CO_2^{2+}/^{44}CO_2^{+}$ ratio was 0.0064, resulting in ~0.1 to 0.25 ‰ contribution to the $^{22}Ne^{+}$ beam.

The KRISS Ne gas analyses were interspersed with air analyses having 2.98 × $10^{-14}$ mol of $^{20}$Ne and a 'standard-sample' bracketing technique was utilized to determine the mass fractionation. The mean $^{20}$Ne beam from the KRISS Ne gas was 54,300 cps while that of the interspersed air standards was 62,700 cps. Air standards run with 1.34 × $10^{-14}$ mol and 2.98 × $10^{-14}$ mol of $^{20}$Ne suggest that the difference in beam size between the KRISS Ne and the interspersed air aliquots could result in a pressure-dependent $^{22}Ne/^{20}Ne$ mass discrimination of $^{22}Ne/^{20}Ne_{@54.3K\ cps}/^{22}Ne/^{20}Ne_{@62.7K\ cps} = 0.99979 \pm 0.00043$ (1σ). While statistically not distinguishable from a value of 1, this potential pressure-dependent mass discrimination factor, along with its uncertainty, was propagated to calculate the final $^{22}Ne/^{20}Ne$ of the atmosphere.

### 2.2.4. University of Tokyo

The standard KRISS Ne gas was first expanded into a 2.1 L tank equipped with a 2 $cm^3$ gas pipette. An aliquot of this gas was expanded to a 2.3 L tank equipped with a 2 $cm^3$ gas pipette. This resulted in a nominal delivery amount of 1.56 × $10^{-10}$ mol $^{20}$Ne (3.49 × $10^{-6}$ $cm^3$ STP). The air sample was collected in the Komaba Campus of University of Tokyo (35°39′46.21" N, 139°41'1.60" E) into a 25 $cm^3$ stainless steel bottle on August 4, 2021. The air was expanded to a 2.1 L tank equipped with a 2 $cm^3$ gas pipette, which results in a nominal delivery amount of 1.74 × $10^{-11}$ mol $^{20}$Ne (3.90 × $10^{-7}$ $cm^3$ STP).

Aliquots of air were admitted to a gas preparation system described earlier (Ebisawa et al., 2004; Kobayashi et al., 2021). The gas was purified with a hot Ti—Zr getter and heavy noble gases (Ar, Kr, Xe) were trapped by a charcoal contained volume kept at the temperature of liquid nitrogen (77 K) for 5 min. The gas was further purified with another hot Ti—Zr getter and two SAES NP10 ZrAl alloy getters for 5 min. Then the sample gas was admitted to the mass spectrometer for analysis. The analysis of the KRISS Ne gas followed the same procedure as that of air.

A VG-3600 noble gas mass spectrometer was used for the analysis. All Ne isotopes and major source of interferences, $^{40}Ar^{+}$ and $^{44}CO_2^{+}$ were measured with a Daly collector with peak-jumping mode (resolution of 200). The $^{40}Ar^{2+}$ and $^{44}CO_2^{2+}$ interferences were kept as low as possible by a sintered-stainless steel filter material in a liquid nitrogen cooled cold finger located close to the ion source. The double- to single-charged ratios of $^{40}Ar^{2+}$ and $^{44}CO_2^{2+}$ ions were determined with a method described in Osawa (2004). The interference contributions from both were <0.04‰ for the KRISS Ne gas and air. Procedural blank level was about 7.59 × $10^{-14}$ mol $^{20}$Ne (1.70 × $10^{-9}$ $cm^3$ STP), which was negligibly small. We noticed no significant pressure dependence of measured Ne isotope ratios observed with $^{20}$Ne amounts admitted to the mass spectrometer ranging from 1.29 × $10^{-13}$ mol (2.89 × $10^{-9}$ $cm^3$ STP) to 2.41 × $10^{-11}$ mol (5.40 × $10^{-7}$ $cm^3$ STP). The KRISS Ne gas and air containing 8.48 × $10^{-12}$ mol $^{20}$Ne (1.90 × $10^{-7}$ $cm^3$ STP) each were analysed and KRISS Ne gas measurements were bracketing an air measurement. No significant memory effect was observed.

## 3. Results and discussion

### 3.1. *Redetermination of atmospheric $^{22}Ne/^{20}Ne$*

Atmospheric $^{22}$Ne/$^{20}$Ne values determined by all participating laboratories are summarised in Fig. 2A-B and Table 4. ATOMKI used the adjacent KRISS Ne gas to calculate the mass fractionation factor and the composition of air from a single aliquot. The ATOMKI data (*n* = 9) vary between 0.10186 ± 0.00001 and 0.10213 ± 0.00003 and overlap despite using two instruments. The data are overdispersed by a factor of 3–10 with respect to uncertainty of the individual data.

The SUERC measurements are relying on a mean mass fractionation factor determined based on a large number of analysis using the KRISS Ne gas prior to analysis of air (see Table 3). This was facilitated by the fast data collection allowed by the automatic operation procedure. Five batches of data were collected. Data from the SUERC#1 (*n* = 19) and SUERC#2 (*n* = 21) air batches used the mass fractionation factor obtained from the first fill of the KRISS Ne gas (1.0227 ± 0.0001) and varying pressure of air from the first fill of the air bottle. These two batches are indistinguishable from each other and from the ATOMKI data, varying between 0.10182 ± 0.00006 and 0.10213 ± 0.00007 and showing little overdispersion (factor of 2–3) relative to individual uncertainties. SUERC#3 (*n* = 29) and SUERC#4 (*n* = 16) air batches used the mass fractionation factor based on the second fill of the KRISS Ne gas (1.0434 ± 0.0001) and varying pressure of air from the first fill of the air bottle. Generally, the uncertainties of these data are the lowest in this batch (0.01%), similar to that of ATOMKI#1. There is 0.05% overdispersion of both batches. These data likely indicate natural variability in the repeatability of analysis, which may be associated with either the gas preparation or the stability of the ion source. Due to the relatively fast data collection using the fully automated system, these data provide an opportunity to further explore the nature of overdispersion and may have the potential in further improving uncertainties with current techniques. SUERC#5 (*n* = 16) shows data of the 2nd air bottle that have been calculated from the mass fractionation factor obtained from the 2nd fill of the KRISS Ne gas. These data also exhibit a very low uncertainty with no overdispersion. The significant reduction of the uncertainty of the individual data from SUERC #1 to #5 may reflect the slow clean-up (few months) of either the cryogenic system or the mass spectrometer or both with respect to trace compounds (such as $^4$He, $N_2$ and $CO_2$). However, we used an analytical method, in which the mass fractionation factor was determined using a large number of analysis of the KRISS gas, prior to the analysis of air. Thus, we can assume that the mass fractionation factor of the mass spectrometer and the analysis of air in SUERC#3–5 batches were carried out in conditions that became increasingly different from each other in time. This may be most apparent in the SUERC#5 batch. Following this logic, a standard bracketing technique would have been a better choice, however the point of this study is to capture the diversity of techniques.

Both UC Davis and the University of Tokyo used a third technique to calculate the atmospheric $^{22}$Ne/$^{20}$Ne. They used two measurements of the KRISS Ne gas that bracketed 1–3 measurements of air. They calculated mean mass fractionation from each KRISS Ne data pair and used the mean of bracketed air measurements (apart from occasions when only one air measurement occurred) to calculate final isotope ratios. It

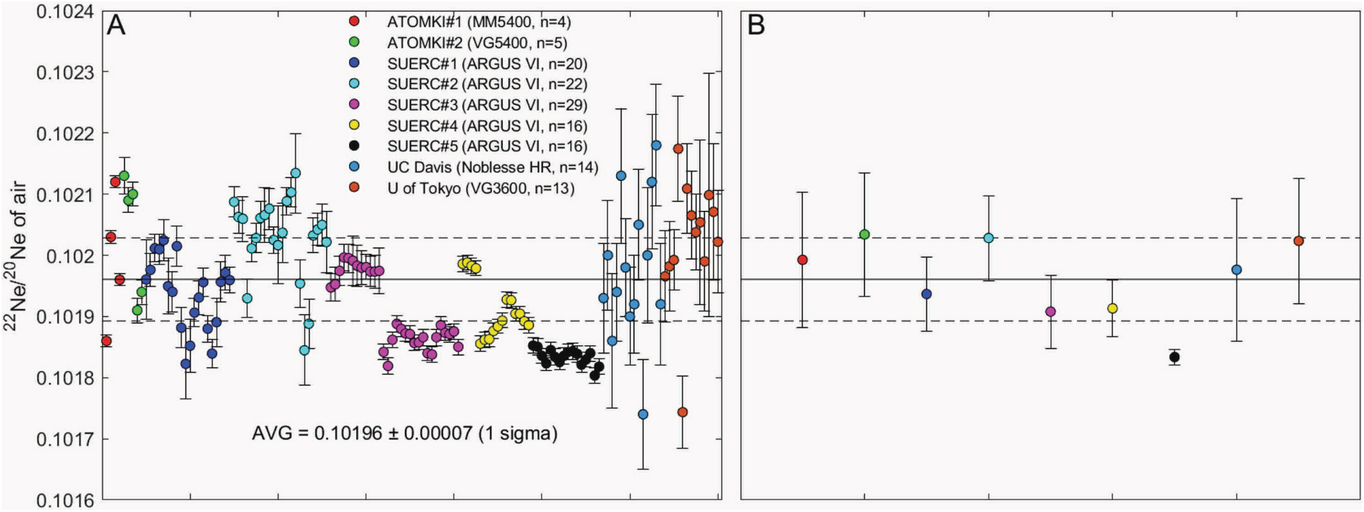

**Fig. 2.** Mass spectrometric results of $^{22}$Ne/$^{20}$Ne of the atmosphere obtained by the analysis of air and the KRISS Ne gas (A) and the mean and standard deviation of each group of data (B). ATOMKI used one KRISS Ne gas to determine a single air value. All ATOMKI data well overlap with each other, with overdispersion of 3–10 times of individual uncertainties. SUERC determined the mass fractionation factor by two batches using two separate fills of the KRISS Ne gas, filled 6 months apart and analysed air from two different air bottles that were filled 4 years apart. SUERC batch numbers (1–5) represents a timely order of analysis. SUERC#1 & #2: Mass fractionation factor from KRISS Ne gas No.1 (1.0227 ± 0.0001), different air pressure from air bottle No.1 (see Table 4). SUERC#3 & #4: Mass fractionation factor from KRISS Ne gas No.2 (1.0434 ± 0.0001) and re-analysis of air bottle No.1 at the same pressure. SUERC #5: Combination of KRISS Ne gas No.2 and air bottle No.2. SUERC#3–5: Extremely small individual uncertainties and large overdispersion is likely due to small variations in gas preparation or the stability of the ion source. Reduction of uncertainty from SUERC#1 - #5 may indicate clean-up of the mass spectrometer's source (see text). Both UC Davis and the University of Tokyo used two measurements of the KRISS Ne gas that bracketed measurements or air and atmospheric $^{22}$Ne/$^{20}$Ne was calculated from mean KRISS Ne values. University of Tokyo and UC Davis data are remarkably similar, exhibiting a mean and standard deviation of 0.1020 ± 0.0001. Degree of uncertainties reflect gas amounts analysed and technique used to calculate air data. UC Davis used 2–4 orders of magnitude less gas in the analysis than anyone else in this study. Solid line: Mean, which is almost identical to the previously published value of 0.1020 ± 0.0008 (Eberhardt et al., 1965). Dashed line: Standard deviation of $^{22}$Ne/$^{20}$Ne of air of 0.10196 (1σ), which is 12 times smaller than that of Eberhardt et al. (1965).

**Table 4**
Results of analysis of the KRISS Ne gas and air and the calculated atmospheric $^{22}Ne/^{20}Ne$ from participating laboratories in this study.

| Laboratory | Measured isotope ratio | | Calculated $(^{22}Ne/^{20}Ne)_{air}$ |
|---|---|---|---|
| | $(^{22}Ne/^{20}Ne)_{KRISS\ Ne\ gas}$ | $(^{22}Ne/^{20}Ne)_{air}$ | |
| ATOMKI #1 (MM5400) | 0.118279 (5) | 0.101341 (4) | 0.10186 (1) |
| Fractionation factor determined individually. For amounts, see notes *. $n_{tot} = 8$. | 0.118175 (4) | 0.101429 (4) | 0.10203 (1) |
| | 0.118121 (3) | 0.101464 (3) | 0.10212 (1) |
| | 0.118086 (3) | 0.101277 (3) | 0.10196 (1) |
| *Mean* | *NA* | *NA* | *0.10199 (11)* |
| ATOMKI #2 (VG5400) | 0.11776 (2) | 0.10117 (2) | 0.10213 (3) |
| Fractionation factor determined individually. For amounts, see ATOMKI #1. $n_{tot} = 10$. | 0.11783 (1) | 0.10119 (1) | 0.10209 (2) |
| | 0.11785 (2) | 0.10121 (1) | 0.10210 (2) |
| | 0.11790 (1) | 0.10107 (2) | 0.10191 (2) |
| | 0.11794 (1) | 0.10114 (1) | 0.10194 (2) |
| *Mean* | *NA* | *NA* | *0.10203 (10)* |
| SUERC #1 (ARGUS VI) | 0.11614 (3) | 0.09970 (6) | 0.10196 (7) |
| Fractionation factor determined by SUERC's KRISS Ne bottle #1 = 1.0227 (1), using aliquots of gas containing $2.69 \times 10^{-12}$ mol $^{20}Ne$ ($6.02 \times 10^{-8}$ $cm^3$ STP) ($n = 16$). | 0.11610 (6) | 0.09971 (2) | 0.10198 (3) |
| | 0.11608 (3) | 0.09975 (2) | 0.10201 (2) |
| | 0.11610 (2) | 0.09974 (2) | 0.10201 (3) |
| Air Ne is determined from the analysis of SUERC's air bottle #1 using $2.24 \times 10^{-12}$ mol $^{20}Ne$ ($5.01 \times 10^{-8}$ $cm^3$ STP) ($n = 20$) corrected for fractionation. | 0.11614 (4) | 0.09976 (3) | 0.10202 (3) |
| | 0.11623 (2) | 0.09969 (4) | 0.10195 (5) |
| | 0.11626 (3) | 0.09968 (3) | 0.10194 (3) |
| Total number of analyses in this batch is $n_{tot} = 36$. (See note **). | 0.11630 (3) | 0.09975 (3) | 0.10201 (3) |
| | 0.11621 (3) | 0.09962 (3) | 0.10188 (3) |
| | 0.11619 (4) | 0.09956 (6) | 0.10182 (6) |
| | 0.11619 (3) | 0.09959 (4) | 0.10185 (4) |
| | 0.11627 (2) | 0.09964 (2) | 0.10191 (2) |
| | 0.11630 (2) | 0.09967 (2) | 0.10193 (3) |
| | 0.11631 (2) | 0.09969 (2) | 0.10196 (2) |
| | 0.11633 (2) | 0.09962 (2) | 0.10188 (2) |
| | 0.11631 (2) | 0.09958 (2) | 0.10184 (2) |
| | – | 0.09963 (4) | 0.10189 (4) |
| | – | 0.09969 (3) | 0.10196 (3) |
| | – | 0.09971 (2) | 0.10197 (3) |
| | – | 0.09970 (2) | 0.10196 (2) |
| *Mean* | *0.11622 (8)* | NA | *0.10194 (6)* |
| SUERC #2 (ARGUS VI) | – | 0.09982 (2) | 0.10209 (2) |
| Fractionation factor determination is as per SUERC #1. Air Ne is determined from the analysis of SUERC's air bottle #1 using $2.98 \times 10^{-12}$ mol $^{20}Ne$ ($6.68 \times 10^{-8}$ $cm^3$ STP) ($n = 22$), corrected for fractionation. | – | 0.09980 (2) | 0.10206 (3) |
| | – | 0.09979 (3) | 0.10206 (4) |
| | – | 0.09967 (3) | 0.10193 (3) |
| | – | 0.09975 (2) | 0.10201 (2) |
| Total number of analyses in this batch is $n_{tot} = 22$. (See note **). | – | 0.09976 (2) | 0.10203 (2) |
| | – | 0.09979 (2) | 0.10206 (3) |
| | – | 0.09980 (4) | 0.10207 (4) |
| | – | 0.09981 (3) | 0.10208 (3) |
| | – | 0.09976 (2) | 0.10202 (2) |
| | – | 0.09975 (6) | 0.10202 (6) |
| | – | 0.09977 (5) | 0.10204 (5) |
| | – | 0.09982 (2) | 0.10209 (2) |
| | – | 0.09984 (2) | 0.10210 (2) |
| | – | 0.09987 (6) | 0.10213 (7) |
| | – | 0.09969 (4) | 0.10195 (4) |
| | – | 0.09958 (5) | 0.10184 (6) |
| | – | 0.09963 (4) | 0.10189 (4) |
| | – | 0.09977 (3) | 0.10203 (3) |
| | – | 0.09978 (2) | 0.10204 (3) |
| | – | 0.09978 (3) | 0.10205 (3) |
| | – | 0.09976 (5) | 0.10202 (5) |
| *Mean* | *0.11622 (8)* | NA | *0.10203 (7)* |
| SUERC #3 (ARGUS VI) | 0.11399 (1) | 0.09771 (2) | 0.10195 (2) |
| Fractionation factor determined by SUERC's KRISS Ne bottle #2 = 1.0434 (1) using aliquots of gas containing $2.69 \times 10^{-12}$ mol $^{20}Ne$ ($6.02 \times 10^{-8}$ $cm^3$ STP) ($n = 19$). | 0.11396 (1) | 0.09772 (2) | 0.10195 (3) |
| | 0.11394 (1) | 0.09774 (2) | 0.10197 (2) |
| | 0.11393 (1) | 0.09776 (2) | 0.10200 (2) |
| Air Ne is determined from the analysis of SUERC's air bottle #1 using $2.24 \times 10^{-12}$ mol $^{20}Ne$ ($5.01 \times 10^{-8}$ $cm^3$ STP) ($n = 30$) corrected for fractionation. | 0.11393 (1) | 0.09776 (2) | 0.10200 (2) |
| | 0.11392 (1) | 0.09775 (4) | 0.10199 (4) |
| | 0.11393 (1) | 0.09775 (3) | 0.10198 (3) |
| Total number of analyses in this batch is $n_{tot} = 49$. (See note **). | 0.11392 (1) | 0.09774 (2) | 0.10198 (3) |
| | 0.11392 (1) | 0.09774 (2) | 0.10198 (2) |
| | 0.11395 (1) | 0.09774 (2) | 0.10197 (2) |
| | 0.11394 (1) | 0.09774 (2) | 0.10197 (3) |
| | 0.11393 (1) | 0.09774 (3) | 0.10197 (4) |
| | 0.11397 (1) | 0.09761 (1) | 0.10184 (1) |
| | 0.11396 (1) | 0.09759 (1) | 0.10182 (1) |
| | 0.11395 (1) | 0.09763 (1) | 0.10186 (1) |
| | 0.11394 (1) | 0.09765 (1) | 0.10189 (1) |
| | 0.11393 (1) | 0.09765 (1) | 0.10188 (1) |
| | 0.11392 (1) | 0.09764 (1) | 0.10187 (1) |

(*continued on next page*)

**Table 4** (*continued*)

| Laboratory | Measured isotope ratio | | Calculated $(^{22}Ne/^{20}Ne)_{air}$ |
|---|---|---|---|
| | $(^{22}Ne/^{20}Ne)_{KRISS\ Ne\ gas}$ | $(^{22}Ne/^{20}Ne)_{air}$ | |
| | 0.11394 (1) | 0.09764 (1) | 0.10187 (1) |
| | – | 0.09762 (1) | 0.10186 (1) |
| | – | 0.09763 (1) | 0.10186 (1) |
| | – | 0.09763 (1) | 0.10187 (1) |
| | – | 0.09761 (1) | 0.10184 (1) |
| | – | 0.09761 (1) | 0.10184 (1) |
| | – | 0.09763 (1) | 0.10187 (1) |
| | – | 0.09765 (1) | 0.10189 (1) |
| | – | 0.09764 (1) | 0.10187 (1) |
| | – | 0.09764 (1) | 0.10187 (1) |
| | – | 0.09764 (1) | 0.10188 (1) |
| | – | 0.09762 (1) | 0.10185 (1) |
| *Mean* | *0.11394 (2)* | *NA* | *0.10191 (6)* |
| SUERC #4 (ARGUS VI) | – | 0.09775 (1) | 0.10199 (1) |
| Fractionation factor determination is as per SUERC #3. | – | 0.09775 (1) | 0.10199 (1) |
| | – | 0.09775 (1) | 0.10198 (1) |
| Air Ne is determined from the analysis of SUERC's air bottle #1 using $2.98 \times 10^{-12}$ mol $^{20}Ne$ ($6.68 \times 10^{-8}$ $cm^3$ STP) ($n = 16$), corrected for fractionation. | – | 0.09774 (1) | 0.10198 (1) |
| | – | 0.09762 (1) | 0.10186 (1) |
| | – | 0.09763 (1) | 0.10186 (1) |
| Total number of analyses in this batch is $n_{tot} = 16$. (See note **). | – | 0.09763 (1) | 0.10186 (1) |
| | – | 0.09764 (1) | 0.10188 (1) |
| | – | 0.09765 (1) | 0.10188 (1) |
| | – | 0.09766 (1) | 0.10189 (1) |
| | – | 0.09769 (1) | 0.10193 (1) |
| | – | 0.09769 (1) | 0.10193 (1) |
| | – | 0.09767 (1) | 0.10190 (1) |
| | – | 0.09767 (1) | 0.10190 (1) |
| | – | 0.09766 (1) | 0.10189 (1) |
| | | 0.09766 (1) | 0.10189 (1) |
| *Mean* | *0.11394 (2)* | *0.097676 (1)* | *0.10191 (5)* |
| SUERC #5 (ARGUS VI) | – | 0.09762 (1) | 0.10185 (1) |
| Fractionation factor determination is as per SUERC #3. | – | 0.09762 (1) | 0.10185 (1) |
| | – | 0.09760 (1) | 0.10184 (1) |
| Air Ne is determined from the analysis of SUERC's air bottle #2 using $2.98 \times 10^{-12}$ mol $^{20}Ne$ ($6.68 \times 10^{-8}$ $cm^3$ STP) ($n = 16$), corrected for fractionation. | – | 0.09759 (1) | 0.10182 (1) |
| | – | 0.09761 (1) | 0.10185 (1) |
| | – | 0.09760 (1) | 0.10183 (1) |
| Total number of analyses in this batch is $n_{tot} = 16$. (See note **). | – | 0.09759 (1) | 0.10183 (1) |
| | – | 0.09760 (1) | 0.10184 (1) |
| | – | 0.09761 (1) | 0.10184 (1) |
| | – | 0.09761 (1) | 0.10184 (1) |
| | – | 0.09761 (1) | 0.10184 (1) |
| | – | 0.09759 (1) | 0.10182 (1) |
| | – | 0.09760 (1) | 0.10183 (1) |
| | – | 0.09761 (1) | 0.10184 (1) |
| | – | 0.09757 (1) | 0.10180 (1) |
| | – | 0.09759 (1) | 0.10182 (1) |
| *Mean* | *0.11394 (2)* | *NA* | *0.10183 (1)* |
| UC Davis (Noblesse HR) | 1.0000 (8) | 0.8576 (8) | – |
| For method, see notes ***. | 1.0003 (8) | 0.8575 (7) | – |
| *Mean* | *1.0001 (5)* | *0.8575 (5)* | *0.10193 (9)* |
| | 1.0006 (8) | 0.8578 (8) | – |
| | 1.0003 (8) | 0.8591 (8) | – |
| *Mean* | *1.0004 (5)* | *0.8584 (5)* | *0.10200 (9)* |
| | 1.0005 (8) | – | – |
| | 1.0003 (7) | – | – |
| *Mean* | *1.0004 (5)* | 0.8572 (8) | *0.10186 (11)* |
| | 1.0012 (7) | 0.8577 (7) | – |
| | 1.0008 (8) | 0.8591 (7) | – |
| *Mean* | *1.0010 (5)* | *0.8584 (5)* | *0.10194 (8)* |
| | 1.0004 (8) | – | – |
| | 0.9998 (8) | – | – |
| *Mean* | *1.0001 (6)* | 0.8592 (7) | *0.10213 (11)* |
| | 1.0012 (8) | 0.8586 (7) | – |
| | 1.0007 (8) | 0.8586 (7) | – |
| | – | 0.8588 (7) | – |
| *Mean* | *1.0010 (6)* | *0.8587 (4)* | *0.10198 (8)* |
| | 1.0006 (8) | 0.8582 (7) | – |
| | 1.0016 (8) | 0.8580 (7) | – |
| *Mean* | *1.0011 (5)* | *0.8581 (5)* | *0.10190 (8)* |
| | 1.0023 (8) | 0.8588 (8) | – |
| | 1.0009 (8) | 0.8583 (7) | – |
| *Mean* | *1.0016 (5)* | *0.8586 (5)* | *0.10192 (8)* |
| | 1.0003 (8) | 0.8592 (7) | – |
| | 1.0015 (8) | 0.8591 (8) | – |

(*continued on next page*)

**Table 4** (*continued*)

| Laboratory | Measured isotope ratio | | Calculated $(^{22}Ne/^{20}Ne)_{air}$ |
|---|---|---|---|
| | $(^{22}Ne/^{20}Ne)_{KRISS\ Ne\ gas}$ | $(^{22}Ne/^{20}Ne)_{air}$ | |
| *Mean* | *1.0009 (6)* | *0.8592 (5)* | *0.10205 (9)* |
| | 1.0032 (9) | 0.8578 (7) | – |
| | 1.0014 (8) | 0.8578 (8) | – |
| *Mean* | *1.0023 (6)* | *0.8578 (5)* | *0.10174 (9)* |
| | 0.9999 (8) | – | – |
| *Mean* | *1.0006 (5)* | 0.8585 (8) | *0.10200 (11)* |
| | 1.0007 (8) | – | – |
| *Mean* | *1.0003 (6)* | 0.8592 (8) | *0.10212 (11)* |
| | 1.0014 | – | – |
| *Mean* | *1.0011 (5)* | 0.8604 (7) | *0.10218 (10)* |
| | 0.9999 (8) | – | – |
| *Mean* | *1.0006 (5)* | 0.8579 (7) | *0.10192 (10)* |
| *Mean* | *NA* | *NA* | *0.10198 (12)* |
| University of Tokyo (VG3600) | 0.12168 (8) | 0.10437 (8) | 0.10197 (7) |
| For method see notes **** | 0.12273 (4) | – | – |
| | 0.12354 (2) | – | – |
| *Mean* | *0.12314 (3)* | 0.10563 (7) | *0.10198 (7)* |
| | 0.12357 (3) | – | – |
| | 0.12345 (6) | – | – |
| *Mean* | *0.12351 (5)* | 0.10596 (3) | *0.10199 (5)* |
| | 0.12069 (8) | – | – |
| | 0.12158 (3) | – | – |
| *Mean* | *0.12113 (6)* | 0.10411 (7) | *0.10217 (9)* |
| | 0.12201 (9) | | |
| *Mean* | *0.12179 (6)* | 0.10424 (3) | *0.10174 (6)* |
| | 0.12218 (3) | – | – |
| *Mean* | *0.12210 (6)* | 0.10487 (5) | *0.10211 (7)* |
| | 0.12234 (6) | – | – |
| *Mean* | *0.12226 (5)* | 0.10497 (6) | *0.10207 (7)* |
| | 0.12249 (4) | – | – |
| *Mean* | *0.12241 (5)* | 0.10507 (5) | *0.10204 (6)* |
| | 0.12171 (25) | – | – |
| | 0.12224 (6) | – | – |
| *Mean* | *0.12197 (15)* | 0.10471 (5) | *0.10205 (13)* |
| | 0.12256 (8) | | |
| *Mean* | 0.12240 (7) | 0.10501 (6) | 0.10199 (8) |
| | – | 0.10512 (20) | 0.10210 (20) |
| | 0.12170 (13) | | |
| | 0.12218 (9) | | |
| *Mean* | 0.12194 (11) | 0.10470 (7) | 0.10207 (11) |
| | 0.12253 (9) | | |
| *Mean* | 0.12235 (9) | 0.10500 | 0.10202 (8) |
| *Mean* | NA | NA | 0.10202 (10) |
| *Global mean $^{22}Ne/^{20}Ne$* | *NA* | *NA* | *0.10196 (7)* |
| *Global mean $^{20}Ne/^{22}Ne$* | *NA* | *NA* | *9.808 (7)* |

Calculated air values were obtained by the multiplication of measured air and the mass fractionation factor, defined as $KRISS_{(real)}/KRISS_{(measured)}$.

NA: Not applicable. $N_{tot}$ refers to the total number of analysis (KRISS + air).

Gas amounts (mol) and volumes ($cm^3$) are converted using standard p (101,325 Pa) and T (273 K) and gas constant of 8.314 J/mol K.

1σ standard deviation of the mean as last significant figures are in parenthesis.

Highly precise and accurate new global mean value (JCGM-200:2012) is recommended to be used.

[*] : ATOMKI: For the KRISS Ne gas 2, 3, 5 and 8 aliquots of gas and for the corresponding air 2, 3, 4 and 7 aliquots of gas were analysed. One aliquot = $1.02 \times 10^{-10}$ mol $^{20}$Ne ($2.29 \times 10^{-6}$ $cm^3$ STP).

[**] : SUERC: Bottle #1 and bottle #2 refer to the 1st and 2nd fill of both KRISS Ne gas and air respectively (see text). Number of the SUERC batches indicates time sequence, analysis #1 being the earliest. Time sequence in SUERC is KRISS #1, Air#1, Air#2, KRISS #2, Air #3, Air #4, Air #5.

[***] : UC Davis: Aliquots containing $1.34 \times 10^{-14}$ mol $^{20}$Ne ($3.0 \times 10^{-10}$ $cm^3$ STP) and $1.16 \times 10^{-14}$ mol $^{20}$Ne ($2.6 \times 10^{-10}$ $cm^3$ STP) were analysed for air and KRISS Ne gas respectively. All $^{20}Ne/^{22}Ne$ values are normalised to the first measurement, which is the first measurement of the KRISS Ne gas (1.0000 (8)). At least one analysis of air is bracketed by two analyses of the KRISS Ne gas. Average of KRISS Ne data pair and air measurements are used to calculate atmospheric $^{22}Ne/^{20}Ne$. Number of analysis is 24 for both KRISS Ne gas and air (total $n = 48$).

[****] : University of Tokyo: Aliquots containing $8.48 \times 10^{-12}$ mol $^{20}$Ne ($1.90 \times 10^{-7}$ $cm^3$ STP) were analysed. KRISS Ne gas measurements ($n = 17$) are bracketing air measurements ($n = 13$). Average of KRISS Ne data pair and air measurements are used to calculate atmospheric $^{22}Ne/^{20}Ne$.

should be noted that UC Davis used the smallest amount of Ne ($1.34 \times 10^{-14}$ mol $^{20}$Ne), two to four orders of magnitude less than that of other laboratories, which played a role in their larger uncertainties. Data from UC Davis ($n$ = 14) and University of Tokyo ($n$ = 13) are remarkably similar. They exhibit an overall mean and standard deviation of 0.1020 ± 0.0001. While these data are slightly more dispersed, they are in a good agreement with all other data overall (Fig. 2B).

Taking all data as one set, with no outliers, the overall mean $^{22}Ne/^{20}Ne$ of air and standard deviation is 0.10196 ± 0.00007 (1σ). This is almost identical to that of Eberhardt et al. (1965) (0.1020 ± 0.0008), although its uncertainty is 12 times smaller. Our study did not verify any other previous determinations (Fig. 3). The value of Valkiers et al. (2008) (0.101975 ± 0.000002) is within error of our value, although it is technically incomparable to other works (see Section 1). We suggest that the new value be used in all geoscience applications. Most existing data would not need to be recalculated due to the very small difference in mean $^{22}Ne/^{20}Ne$ values.

The gravimetric method contributes only 15% of the overall

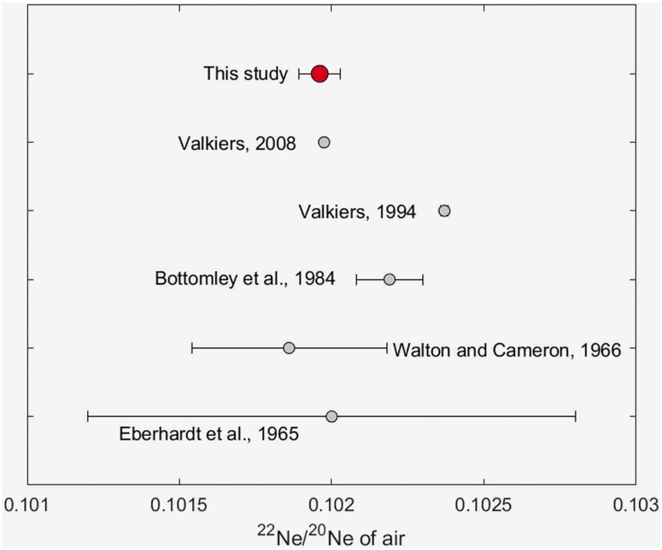

**Fig. 3.** Summary of atmospheric $^{22}Ne/^{20}Ne$ determinations. Results of this study (0.10196 ± 0.00007, red) obtained by the combination of gravimetry and mass spectrometry from four laboratories, are nearly identical to the $^{22}Ne/^{20}Ne$ of air of the most commonly used reference work of Eberhardt et al. (1965) (0.1020 ± 0.0008), although with a 12 times less uncertainty. Our results are also identical to that of Valkiers et al. (2008) (0.101975 ± 0.000002), although their value is technically incomparable to others' (see main text). Our study was unable to verify the highly precise value of Valkiers et al. (1994) (0.10237 ± 0.00001) or that of any other less recent works. Uncertainties are 1σ standard deviations. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

uncertainty, the remaining 85% originating from the overall reproducibility of Ne isotope measurements. The dispersion of the majority of data (except SUERC#3,4,5) is in an excellent agreement. This suggests that the quality of data that has been obtained at a relatively high partial pressure in the mass spectrometer is not governed by the technique and analytical method and that limitations have been reached. Having said that, SUERC#3–5 datasets imply that significant improvement in the repeatability of data may be achieved. Had data collection in the SUERC#3–5 batches applied the technique of UC Davis (standard bracketing), further improvement to the level of sub 0.1% in the uncertainty of $^{22}Ne/^{20}Ne$ of air could have been achieved.

### 3.2. *Revisiting the atmospheric $^{21}Ne/^{20}Ne$*

The accuracy and precision of the atmospheric $^{21}Ne/^{20}Ne$ ratio is particularly important for techniques such as cosmogenic Ne dating (Ma and Stuart, 2018 and references therein). While in theory the preparation of a binary gas mixture of $^{21}Ne$ and $^{20}Ne$ (or $^{22}Ne$) from pure single isotope sources and its gravimetric $^{21}Ne/^{20}Ne$ (or $^{21}Ne/^{22}Ne$) determination would be possible, the use of such a gas in better constraining the atmospheric $^{21}Ne/^{20}Ne$ would be exceedingly expensive and has a significant limitation. The composition of that gas would have to be close to that of air ($^{21}Ne/^{20}Ne = 0.002959$ and $^{21}Ne/^{22}Ne = 0.029$, this study and Györe et al. (2019)) to overcome linearity issues in mass spectrometers. The $^{21}Ne/^{20}Ne$ ratio in this case would be even smaller than $^{36}Ar/^{40}Ar$ of air (0.0033, Lee et al. (2006)). This suggests that the propagated relative uncertainty of the $^{21}Ne/^{20}Ne$ and $^{21}Ne/^{22}Ne$ of gravimetrically determined gases would exceed ~0.1% and ~ 0.01%, respectively.

Recent advances in noble gas mass spectrometry, however, have demonstrated that atmospheric $^{21}Ne/^{20}Ne$ and $^{21}Ne/^{22}Ne$ can be repeated with 0.03–0.14% (Györe et al., 2021a; Györe et al., 2019; Honda et al., 2015; Saxton, 2020; Wielandt and Storey, 2019). This means that the source of uncertainty from gravimetry when preparing the above Ne isotope mixture would overtake that of mass spectrometric analysis.

All of the recent atmospheric $^{21}Ne/^{20}Ne$ determinations relied on the $^{22}Ne/^{20}Ne$ of 0.1020 ± 0.0008 (Eberhardt et al., 1965). The new $^{22}Ne/^{20}Ne$ value can be used to recalculate the mean atmospheric $^{21}Ne/^{20}Ne$ of five previous studies following Eq. (5).

$$\left[\frac{\sqrt{\frac{M_{20Ne}}{M_{22Ne}}}-1}{\sqrt{\frac{M_{20Ne}}{M_{21Ne}}}-1}\right]\left[\frac{\left(\frac{^{21}Ne}{^{20}Ne}\right)_{measured}}{\left(\frac{^{21}Ne}{^{20}Ne}\right)_{air}}-1\right]=\left[\frac{\left(\frac{^{22}Ne}{^{20}Ne}\right)_{measured}}{\left(\frac{^{22}Ne}{^{20}Ne}\right)_{air}}\right]-1 \qquad (5)$$

The effect of the new atmospheric $^{22}Ne/^{20}Ne$ value on the atmospheric $^{21}Ne/^{20}Ne$ ratios is negligible (Table 5). The improvement in accuracy is significant.

### 3.3. *Creative ways of using a high purity Ne gas*

The artificial Ne mixture prepared for this study is a valuable gas that has potential use as a research tool. Despite the most recent developments in noble gas mass spectrometry that allowed mostly interference free $^{22}Ne$ isotope measurements, there is still room for reducing

**Table 5**
Recalculated atmospheric $^{21}Ne/^{20}Ne$ values based on the new reference value of $^{22}Ne/^{20}Ne = 0.10196 \pm 0.00007$, obtained from this study and including the error on the atmospheric $^{21}Ne/^{20}Ne$.

| Publication | Published $(^{21}Ne/^{20}Ne)_{air}$ using $(^{22}Ne/^{20}Ne)_{air} = 0.102$ which did not include error of $(^{22}Ne/^{20}Ne)_{air}$. | Published $^{21}Ne/^{22}Ne$ | *Re*-calculated $(^{21}Ne/^{20}Ne)_{air}$ using |
|---|---|---|---|
| | | | $(^{22}Ne/^{20}Ne)_{air} = 0.10196$ which includes error from new $(^{22}Ne/^{20}Ne)_{air}$. |
| Györe et al. (2019)* | 0.002959 (4) | NA | 0.002958 (25) |
| Honda et al. (2015) | 0.002905 (3) | NA | 0.002904 (3) |
| Wielandt and Storey (2019) | 0.0029577 (7) | NA | 0.002957 (17) |
| Saxton (2020) | 0.0029356 (5) | NA | 0.002937 (1) |
| Heber et al. (2009)** | NA | 0.02878 (9) | 0.002934 (9) |
| Györe et al. (2019)*** | 0.002959 (2) | NA | 0.002964 (21) |

1σ uncertainties as last significant figures are in parenthesis.
For molar masses when correcting for fractionation (Eq. (5)) see Table 3.
NA: Not applicable.
* : Best Gaussian fit instead of mean as per published value.
** : Eq. (5). is not applied. New ratio is calculated by the multiplication of their atmospheric $^{21}Ne/^{22}Ne$ and the $^{22}Ne/^{20}Ne$ of this study. Their atmospheric $^{21}Ne/^{22}Ne$ value relies on assumptions on mass fractionation and its error may not represent the repeatability of $^{21}Ne/^{22}Ne$ measurements. Thus, no change in the error when including that of $^{22}Ne/^{20}Ne$ of this study is observed.
*** : Values have been recalculated from the original dataset using weighted mean and error of weighted mean instead of best Gaussian fit, to be consistent with other works.

uncertainty on air-free $^{22}$Ne ($^{22}$Ne*) quantification. In cosmogenic Ne applications, this arises from the large air correction for $^{22}$Ne (Farley et al., 2020). Spiking samples that have low cosmogenic or nucleogenic $^{22}$Ne content with an accurately known amount of pure $^{22}$Ne (standard addition) in a way that very little $^{21}$Ne is added can be the way forward. The artificial Ne standard presented in this study with its precisely and accurately known $^{22}$Ne/$^{20}$Ne (0.11888 ± 0.00001) and very high $^{22}$Ne/$^{21}$Ne of 541.3, provides so far, the most precise, accurate, easy and cost-effective method. The reduction of uncertainty of $^{22}$Ne/$^{20}$Ne by above technique has the potential to increase resolution of cosmogenic vs. crustal derived Ne (Espanon et al., 2014) or to detect small deviation from cosmogenic spallation lines (see e.g. Vermeesch et al., 2015).

Highly repeatable neon isotopic determinations of geological materials relies on the cryogenic separation of He and Ne (Hiyagon, 1989). The calibration of such a process in many laboratories is carried out with air which has a Ne/He ratio (3.47, Ozima and Podosek (2002) that is much higher than most natural gas samples which can have Ne/He $<$0.0002 (e.g. Scott et al., 2021). While calibration gases with purpose-prepared low Ne/He are common (Farley et al., 2020; Péron et al., 2019), the isotopic fractionation of Ne in the presence of trace He remains poorly understood. With increasing precision of Ne isotope ratio determinations (Farley et al., 2020; Györe et al., 2021a) there is a need to reduce generally observed overdispersion of ratio repeatability with respect to individual uncertainties of data (see Section 3.1 and Fig. 2). Our artificial Ne mixture has $^{4}$He/$^{22}$Ne $= 7.23 \times 10^{-5}$, several orders of magnitude lower than air (3.12), while the $^{22}$Ne/$^{21}$Ne = 541.3 is much higher than air (34.5). A calibration gas with varying ratio of this gas and air would allow the development of series of standards easily with varying He/Ne and $^{22}$Ne/$^{21}$Ne content and allow quantification of isotope fractionation with respect to trace He content.

The uncertainties of the individual data from the MM5400 mass spectrometer (ATOMKI 1 data) are almost identical to that of a state-of-the-art ARGUS VI noble gas mass spectrometer (SUERC #3–5 data). While the overdispersion of the ATMOKI 1 data is slightly larger than exhibited by SUERC #3–5 dataset, they are within the same order of magnitude. The fast data acquisition in SUERC provides an opportunity to tackle changes in isotope ratio values with a much higher resolution in time. This opens the door to better understand the nature and reasons for observed overdispersions in almost all noble gas mass spectrometers.

The combination of the above approach with fast data collection may be important for samples that cannot be easily replicated in multiple laboratories due to limited sample availability such as lunar basalts (Nottingham et al., 2022).

## 4. Conclusions

Here we present the most comprehensive and robust redetermination of an atmospheric noble gas isotope ratio to date. An artificial, high purity mixture of $^{22}$Ne and $^{20}$Ne has been prepared (KRISS Ne gas) whose $^{22}$Ne/$^{20}$Ne has been determined gravimetrically to be 0.11888 ± 0.00001 (0.01%, 1σ) (equivalent of $^{20}$Ne/$^{22}$Ne of 8.4118 ± 0.0007). Four laboratories used this Ne isotope mixture to determine the global $^{22}$Ne/$^{20}$Ne of the atmosphere using aliquots of air and a variety of mass spectrometric techniques. The ($^{22}$Ne/$^{20}$Ne)$_{\mathrm{air}}$ is 0.10196 ± 0.00007 (0.07%, 1σ) (equivalent of $^{20}$Ne/$^{22}$Ne of 9.808 ± 0.007) based on a total of 149 analysis of air and 85 analysis of the KRISS Ne gas. This new value overlaps with the most commonly used atmospheric $^{22}$Ne/$^{20}$Ne of 0.1020 ± 0.0008 (Eberhardt et al., 1965) although its uncertainty is 12 times smaller. The gravimetric method only contributes 15% to the overall reproducibility of data, which suggests that there is still way of improving uncertainty by the reduction measurement repeatability.

We used this new air $^{22}$Ne/$^{20}$Ne to re-calculate the atmospheric $^{21}$Ne/$^{20}$Ne of five earlier works that based their value on previous atmospheric $^{22}$Ne/$^{20}$Ne values. Although the absolute values have not changed significantly, we put a lot more confidence into the accuracy of the atmospheric $^{21}$Ne/$^{20}$Ne. Since the mean value of both the new air $^{22}$Ne/$^{20}$Ne and recalculated $^{21}$Ne/$^{20}$Ne are not significantly different from the widely accepted values adopting the new values does not require recalculation of existing data. The unique elemental ($^{4}$He/$^{22}$Ne $= 7.23 \times 10^{-5}$ vs. ($^{4}$He/$^{22}$Ne)$_{\mathrm{air}}$ = 3.12) and isotopic ($^{22}$Ne/$^{21}$Ne = 541.3 vs. ($^{22}$Ne/$^{21}$Ne)$_{\mathrm{air}}$ = 34.5) composition of the high purity Ne isotope mixture has the potential to reduce the uncertainty of Ne isotope determinations.

Those interested in acquiring the pure artificial Ne gas should contact either the corresponding author or Inseok Yang (iyang@kriss.re.kr).

## Author contribution

Conceptualization: H.S., D.G. Preparation of the artificial Ne gas, gravimetry, metrology, and supply of the artificial Ne gas: I.Y. Laboratory analysis and calculations: All authors. First draft: D.G. Writing and editing: All authors.

## CRediT authorship contribution statement

**Domokos Györe:** Conceptualization, Formal analysis, Methodology, Writing – original draft, Writing – review & editing, Data curation, Investigation, Visualization. **Hirochika Sumino:** Conceptualization, Formal analysis, Methodology, Writing – review & editing. **Inseok Yang:** Formal analysis, Methodology, Resources, Validation, Writing – review & editing, Data curation. **László Palcsu:** Formal analysis, Methodology, Writing – review & editing. **Elemér László:** Formal analysis, Methodology, Writing – review & editing. **M. Cole Bishop:** Formal analysis, Methodology, Writing – review & editing. **Sujoy Mukhopadhyay:** Data curation, Formal analysis, Methodology, Writing – review & editing. **Finlay M. Stuart:** Data curation, Methodology, Writing – review & editing.

## Declaration of Competing Interest

Significant part of the analytical work in this study was carried out on an instrument manufactured by Thermo Fisher Scientific, which Isomass Scientific Inc. is the official distributor of within Canada. Isomass Scientific Inc. does not have any direct benefit from the publication of this work.

## Data availability

All data presented in this work are available in data tables within this submission.

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