Article

New System for Measuring Cosmogenic Ne in Terrestrial and Extra-Terrestrial Rocks

Domokos Györe * , Luigia Di Nicola, David Currie and Finlay M. Stuart

Scottish Universities Environmental Research Centre (SUERC), East Kilbride G75 0QF, UK;
Luigia.DiNicola@glasgow.ac.uk (L.D.N.); d.currie.1@research.gla.ac.uk (D.C.); fin.stuart@glasgow.ac.uk (F.M.S.)
* Correspondence: Domokos.Gyore@glasgow.ac.uk

Abstract: Cosmogenic Ne isotopes are used for constraining the timing and rate of cosmological and Earth surface processes. We combined an automated gas extraction (laser) and purification system with a Thermo Fisher ARGUS VI mass spectrometer for high through-put, high precision Ne isotope analysis. For extra-terrestrial material with high cosmogenic Ne concentrations, we used multi-collection on Faraday detectors. Multiple measurements (n = 26) of 1.67×10^{-8} cm^3 air-derived ^{20}Ne yielded an uncertainty of 0.32%, and ^{21}Ne/^{20}Ne = 0.17% and ^{22}Ne/^{20}Ne = 0.09%. We reproduced the isotope composition of cosmogenic Ne in the Bruderheim chondrite and Imilac pallasite in a sub-ten mg sample. For lower Ne amounts that are typical of terrestrial samples, an electron multiplier detector was used in peak jumping mode. Repeated analysis of 3.2×10^{-11} cm^3 STP ^{20}Ne from air reproduced ^{21}Ne/^{20}Ne and ^{22}Ne/^{20}Ne with 1.1% and 0.58%, respectively, and ^{20}Ne intensity with 1.7% (n = 103) over a 4-month period. Multiple (n = 8) analysis of cosmogenic Ne in CREU-1 quartz yielded $3.25 \pm 0.24 \times 10^8$ atoms/g (2 s), which overlaps with the global mean value. The repeatability is comparable to the best data reported in the international experiments performed so far on samples that are 2–5× smaller. The ability to make precise Ne isotope determinations in terrestrial and extra-terrestrial samples that are significantly smaller than previously analysed suggests that the new system holds great promise for studies with limited material.

Keywords: cosmogenic ^{21}Ne; noble gas isotope; mass spectrometry; neon isotope; ^{21}Ne; Ne dating; Bruderheim chondrite; Imilac pallasite; CREU quartz; cosmogenic nuclides

1. Introduction

Cosmogenic Ne was proven to be an adept recorder of the timing and rates of surface processes on the Earth and Moon [1–3] and the time of meteorite release from parent bodies [4]. Precise determination of neon isotopes in rocks and minerals are conventionally made using static gas magnetic sector mass spectrometers [5–8]. The low production rate at the Earth's surface and the presence of isobaric interferences at all Ne isotopes means that precise determination of terrestrial cosmogenic Ne is routinely measured in only a handful of laboratories worldwide [5]. Improvements in mass spectrometry in the last ten years, in particular the ability to resolve some of main isobaric interferences [8–10], will lead to better and faster cosmogenic Ne determinations.

Here, we report the use of a Thermo Fisher ARGUS VI mass spectrometer with an automated gas extraction and purification system for the determination of cosmogenic Ne in both extra-terrestrial and terrestrial material. It is a low resolution instrument [11], which requires low background levels and a good understanding of isobaric interferences [6]. Where these can be obtained, the high sensitivity and good instrument stability combine to allow high throughput cosmogenic Ne determinations on samples that are analysed by conventional instruments. Two protocols can be applied depending on Ne concentrations: multi-collection using Faraday detectors and peak-jumping mode using a compact discrete dynode (CDD) detector. We demonstrate the multi-collection Faraday technique with new analysis of cosmogenic Ne in sub-ten mg samples of Bruderheim chondrite and Imilac

pallasite and the peak-jumping CDD analysis of 19.9 mg aliquots of CREU-1 quartz. We use this study to demonstrate how significant reduction in sample size affects uncertainty and the implication of that in cosmogenic Ne dating.

2. Analytical System

The Thermo Fisher ARGUS VI is a low resolution (R < 200), small volume (0.7 litre) 6-detector static vacuum mass spectrometer designed primarily for Ar isotope analysis [12]. It was recently shown to be capable of making high precision determinations of Ne, Kr and Xe isotopes [6,11,12]. The need to minimise isobaric interferences for Ne isotope determinations demanded several modifications to the mass spectrometer vacuum envelope. Gas equilibrated with the mass spectrometer is forced to enter the ion source via a SAES GP50 ZrAl alloy getter held at room temperature in order to minimise the H_2^+ level, which controls the rate of formation of Ar^{2+} and CO_2^{2+} [13], as well as $^{20}NeH^+$ [6]. A charcoal-filled finger on the source block is cooled with liquid nitrogen during analysis to reduce the level of residual Ar and CO_2 in the mass spectrometer.

The ion source operates at 4.5 kV acceleration potential, 250 µA trap current and 80 eV electron energy to minimise NeH^+ production in the source [6]. The source parameters (ion repeller voltage, extraction, focus and symmetry) were tuned for maximum sensitivity using ^{20}Ne. The magnet position was set to achieve the coincidence of the flat-topped peaks of all Ne isotopes (^{20}Ne, ^{21}Ne and ^{22}Ne) on the Faraday detectors (10^{12} Ohm resistance amplifiers), and of ^{22}Ne and ^{21}Ne on the combination of Faraday and a compact discrete dynode (CDD) detector, respectively (Figure 1). The release of CO_2 from the CDD requires that it is conditioned. In the initial phase of this work, the CDD was bombarded by a CO_2 beam and pumped by the mass spectrometer ion pump for several weeks. This resulted in a reduction in the dynamic CO_2 beam intensity from >100 fA to a normal operating level of 2.5 fA.
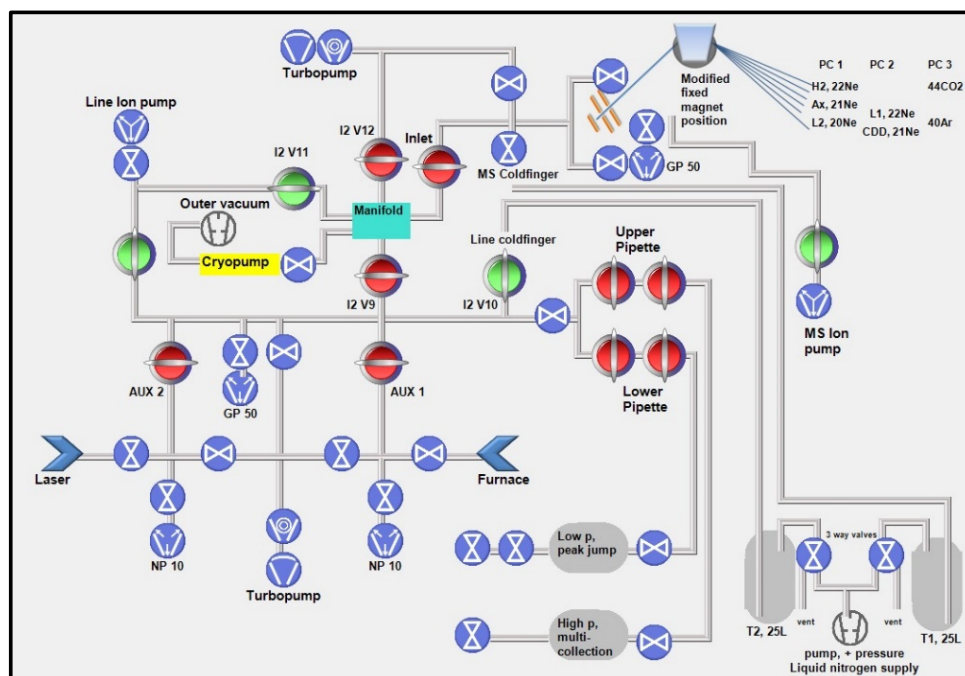
Figure 1. Schematic picture of the fully automatized Thermo Fisher ARGUS VI mass spectrometer and preparation system in SUERC. Two 2L air reservoirs, each equipped with a 0.1 cm^3 gas pipette, provided the means for calibration. The magnet position allowed multi collecting of Ne isotopes. PC1: (H2: ^{22}Ne—Ax: ^{21}Ne—L2: ^{20}Ne). PC2: (L1: ^{22}Ne—CDD: ^{21}Ne). PC3: (H2: $^{44}CO_2$—L2: ^{40}Ar). Blue valve: manual. Green: pneumatically actuated, open. Red: pneumatically actuated, closed. PC: peak coincidence.

High precision Ne isotope analysis is complicated by isobaric interferences at all peaks. Although new instruments can either fully or partially resolve some of the common interferences [8,9], in many cases, a correction is required [6,7,10,14,15]. This requires the measurement of several other peaks, which has an implication on measurement time and data precision. The optimisation of analysis procedures in mass spectrometer control software (Qtegra) required the use of four lab books, starting with hydrogen, followed by mass 18, 19, 40 and 44, prior to the analysis of Ne isotopes (Figure 2). The number of cycles required for Ne isotope analysis was optimised to overcome uncertainty introduced by the time delay. We developed both a multi-collection mode using the array of Faraday detectors where the smallest Ne beam was greater than ~7 fA and a peak jumping mode that used the CDD for smaller Ne beam intensities.
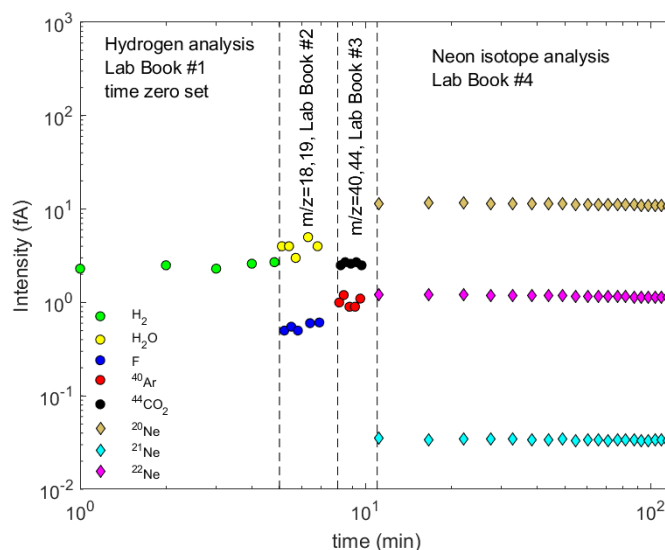
Figure 2. Schematic of the measurement protocol for high precision Ne analysis using the Thermo Fisher ARGUS VI mass spectrometer. The analysis was performed in four lab books in Qtegra to minimise magnet current movement when Ne isotopes were measured. Interfering compounds and hydrogen were measured first for 10 min. Ne isotope measurements were long enough to overcome the uncertainty introduced by the time gap.

3. Cosmogenic Ne in Extra-Terrestrial Material: Multi-Collection Faraday Technique

The multi-collection Faraday mode was developed for the determination of the $^{21}Ne/^{20}Ne$ of air [6] and precise analysis of the Ne isotope composition of natural gases [14]. The high sensitivity of the ARGUS system allowed this procedure to be used to determine cosmogenic Ne in small samples of extra-terrestrial material. Here, we report Ne isotopes in small samples (4.1 to 10.7 mg) of Bruderheim L-chondrite and the Imilac pallasite in order to establish the precision of Ne isotope determinations in meteorites.

Repeated analysis of air standard (n = 26) over the two-week analysis period yielded repeatability values of $^{21}Ne/^{20}Ne$ and $^{22}Ne/^{20}Ne$ of 0.17% and 0.09%, respectively (1σ), calculated by fitting a best Gaussian curve to the probability density distribution [15]. All isotope data are consistent with the combination of mass fractionation of air and the presence of NeH^+, as described earlier [6]. The repeatability of the intensity of ^{20}Ne (~3450 fA) was 0.32%. Isobaric interferences from $^{40}Ar^{2+}$ and $^{44}CO_2{}^{2+}$ were trivial (less than 0.3‰) and all other interferences were significantly smaller than 0.1‰ [6].

The meteorite samples were heated to 1500 °C for 10 min in a double-walled furnace. The gas purification and Ne isotope analysis were conducted using methods described earlier [16]. Furnace hot blanks were measured and the Ne isotopic composition was found to be isotopically indistinguishable from air, albeit less than 0.3% of sample beam intensities. All samples were reheated, which confirmed that all Ne was extracted in the heating step. For these analyses, we did not routinely monitor H_2O^+ and HF^+ as

beam intensities were so low that it had a negligible (<0.1‰) effect on $m/z = 20$. While $^{20}NeH^+$ generation in the mass spectrometer ion source was significant for analyses of terrestrial Ne at partial pressures that are similar to those determined here, in this study, the contribution at $m/z = 21$ was insignificant as $^{21}Ne^+$ abundances in meteorites were approximately 30 times higher. We estimate that the $^{20}NeH^+$ contribution for $^{21}Ne^+$ was less than 0.1‰ in the meteorite analyses reported here.

The Ne isotope data for both meteorite samples are presented in Table 1 and Figure 3. The two Bruderheim samples yielded $^{20}Ne/^{22}Ne$ of 0.867 ± 0.002 and 0.852 ± 0.002 and $^{21}Ne/^{22}Ne$ values of 0.916 ± 0.002 and 0.925 ± 0.002. These plotted within the range determined by earlier studies ([15,16], (T. Graf, pers. comm.)), thus confirming our ability to replicate existing data. The difference in $^{21}Ne/^{20}Ne$ ratios of the two samples was small, but beyond the analytical uncertainty of each measurement. This may reflect variation in the contribution of the primordial Ne component within the samples. The Bruderheim sample had a well-established ^{22}Ne concentration of $12.14 \pm 0.11 \times 10^{-8}$ cm^3 STP/g (personal communication with T. Graf). On this basis, using our measurements, we calculated an instrument sensitivity of $5.01 \pm 0.06 \times 10^{-12}$ cm^3 STP Ne/fA, which was equivalent to $1.25 \pm 0.02 \times 10^{15}$ cps/cm^3 STP (where 1 cps = 1.6×10^{-19} A).

The isotopic compositions of Ne for the two samples of Imilac pallasite were indistinguishable from each other. The $^{20}Ne/^{22}Ne$ values were 0.896 ± 0.002 and 0.893 ± 0.002 and the $^{21}Ne/^{22}Ne$ values were 1.028 ± 0.003 and 1.030 ± 0.003. These values were extremely close to those determined earlier for the Imilac pallasite [17] (Figure 3). The measured ^{22}Ne concentrations of 66.52 ± 0.08 and $69.42 \pm 0.07 \times 10^{-8}$ cm^3 STP/g overlapped that of earlier determinations ($66.0 \pm 3.6 \times 10^{-8}$ cm^3 STP ^{22}Ne/g) [17].

The precision of the Ne isotope ratios of both meteorites was ± 0.2–0.3%. This was ~50–100 and 5–10 times greater than the precision of $^{20}Ne/^{22}Ne$ and $^{21}Ne/^{22}Ne$ measurements of air, and was slightly higher than the repeatability of the air measurements (0.17% and 0.09% for $^{20}Ne/^{22}Ne$ and $^{21}Ne/^{22}Ne$, respectively). We explain this by the large amount of matrix present in the gas phase after melting of the mineral. The intensity determinations had an uncertainty of $\pm$ 0.02% at signal sizes of 200 fA, and this was identical to the precision of ^{22}Ne beams of a similar size (~335 fA) derived from air calibrations.

Table 1. Neon isotope data of newly measured meteorites.

Sample	Weight (mg)	$^{20}Ne/^{22}Ne$	$^{21}Ne/^{22}Ne$	^{22}Ne
		This study		
Bruderheim-1	9.13	0.867 (2)	0.916 (2)	N/A
Bruderheim-2	10.67	0.852 (2)	0.925 (2)	N/A
Imilac-1	10.10	0.896 (2)	0.893 (2)	66.52 (8)
Imilac-2	4.10	1.028 (3)	1.030 (3)	69.42 (7)
		Pers. comm. with T. Graf		
Bruderheim-1	49.2	0.914	0.851	11.98
Bruderheim-2	42.2	0.914	0.850	12.30
Bruderheim-3	25.5	0.911	0.844	12.18
Bruderheim-4	33.0	0.912	0.842	12.20
Bruderheim-5	24.3	0.912	0.849	12.15
Bruderheim-6	53.7	0.918	0.839	11.99
Bruderheim-7	32.8	0.922	0.828	12.12
Bruderheim-8	33.4	0.925	0.839	12.21

1σ are shown in parenthesis as last significant figures. Ne isotope concentrations are in cm^3 STP/g $\times 10^8$ where $p = 0.101$ MPa and T = 0 °C in accordance with [20]. N/A: not applicable as the Bruderheim, in this study, was used to determine mass spectrometer sensitivity using data from T. Graf (pers. comm.). Errors of data obtained from pers. comm. with T. Graf were not provided.
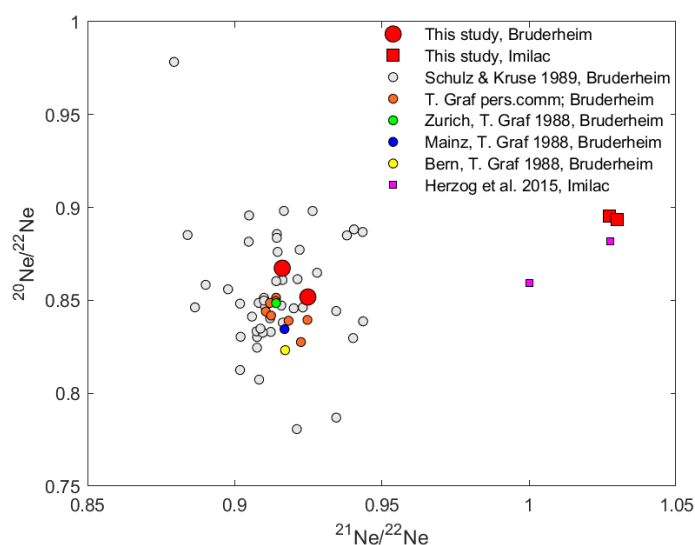
Figure 3. Neon isotopic composition of Bruderheim chondrite and Imilac pallasite analysed using ARGUS VI mass spectrometer. Bruderheim data overlapped with earlier determinations. Slight deviations in between the measurements may indicate variation in the contribution of primordial components. Imilac data overlapped with each other within the measurement error for both isotope ratios, and overlapped with earlier determinations. Measurement uncertainties are smaller than symbols. Other data are from Refs. [17–19] and personal communication with T. Graf.

Our data were obtained from a significantly smaller sample than earlier studies. The direct comparison of the quality of our data to earlier determinations is difficult because of the low number of analyses and the absence of precision in previous works. Our Bruderheim chondrite samples (9.1 and 10.7 mg) were between 2 and 6 times smaller than most recent measurements (T. Graf pers. comm.). Our Imilac pallasite samples (4.1 and 10.1 mg) were at least half the size of earlier determinations [17]. Incorporating the repeatability of air Ne isotope ratios into the overall isotope ratio uncertainty (~0.5%), we found a four-fold improvement on those measured in samples that were of at least 2–5 times greater mass [17].

## 4. Cosmogenic Ne in Terrestrial Material: Analysis by Peak Jumping Using Electron Multiplier

4.1. Analysis Procedure and Repeated Measurement of Low Quantities of Atmospheric Ne

The concentration of Ne in terrestrial rocks and minerals is significantly less than in meteorites, and typically requires the use of electron multiplier detectors [8–10]. We developed a peak jumping protocol using the CDD detector that was located in the L3 position. The peak measurement sequence followed that described above (Figure 2). Hydrogen ($m/z = 2$) and background ($m/z = 2.2$) were measured on the L2 Faraday detector with all other isotopes determined on the CDD. No NeH^+ was recorded during analysis, in line with findings using a Noblesse-HR at a similarly low Ne partial pressure [7].

Over the course of 4 months, the blanks were composed of fractionated air (n = 36). Isobaric interference from HF^+ always stayed below 1‰. Contributions at $m/z = 20$ from $H_2^{18}O^+$ (~1%) and $^{40}Ar^{++}$ (~5%) were small. In contrast, $^{44}CO_2^{++}$ dominated $m/z = 22$. The air-like blank in the mass spectrometers rendered blank correction for cosmogenic Ne redundant.

Calibration data (n = 103) were collected over the course of 4 months from aliquots of air at the level of $9.36 \pm 0.21 \times 10^{-14}$ cm^3 STP ^{21}Ne, which was equivalent to ^{21}Ne from 7.7 mg CREU quartz. The repeatability of the ^{21}Ne/^{20}Ne and ^{22}Ne/^{20}Ne of air was 1.10% and 0.62%, respectively (Figure 4) (1σ, 2 outliers), which was calculated by fitting a best-fit Gaussian curve to the probability density distribution. The isobaric interferences from H_2O^+, HF^+ and $^{40}Ar^{2+}$ at $m/z = 20$, $^{63}Cu^{3+}$ at $m/z = 21$ and $^{66}Zn^{3+}$ at $m/z = 22$ were trivial.

Interference from organic compounds was assumed to be negligible [6]. The contribution of CO_2^{2+} at m/z = 22 averaged around 7% over the 4-month period. Singly/doubly charged component determinations followed earlier practice [6]. The isotope ratios plotted slightly to the right of the mass fractionation line in Figure 4, indicating either a constant excess at m/z = 21 (termed excess Ne) (horizontal movement in Figure 4), which does not appear in the blank measurements, or a different CO_2 contribution to that of the dynamic blanks (vertical movement in Figure 4). However, doubly charged CO_2 would only increase with increasing partial pressure in the mass spectrometer [13,21], which would move our data to the lower ^{22}Ne/^{20}Ne regimes and would not explain our data. Therefore, we suggest the presence of excess Ne.
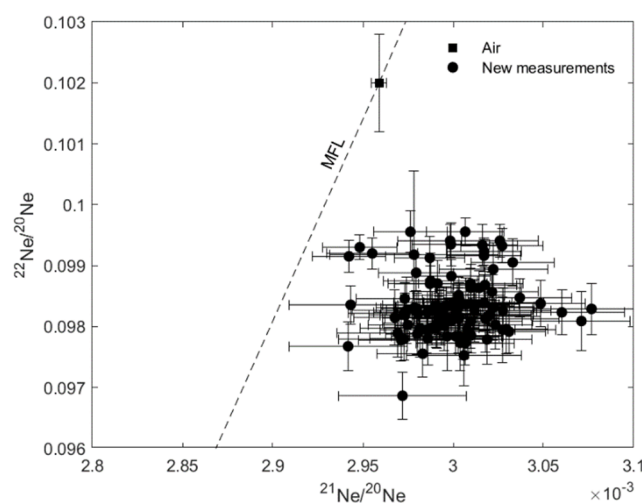
Figure 4. Ne isotope ratio from the repeated analysis of air using the ARGUS VI mass spectrometer. The delivery amount was $9.36 \pm 0.21 \times 10^{-14}$ cm³ STP ^{21}Ne/aliquot, equivalent of ^{21}Ne from 7.7 mg CREU. The repeatability of ^{21}Ne/^{20}Ne was 1.1% (1σ) (n = 103), which was a significant achievement at this partial pressure of Ne. The repeatability of ^{22}Ne/^{20}Ne was 0.62% and was likely governed by the 7% CO_2 correction at mass 22. All data were located slightly right of the mass fractionation line (MFL), indicating a constant excess at m/z = 21, which was unchanged over an order of magnitude of Ne partial pressure and was corrected out (see text). Air is from Refs. [6,22]. Plotted uncertainties are 1σ.

Excess Ne, or, more precisely, excess mass 21 is the result of the liberation of material inside the mass spectrometer by the calibration (or sample) beam. This was not detected on the Faraday detectors at higher beam intensities, and the fact that the CDD is known to produce CO_2 implies that the electron multiplier is the source [6]. Test measurements revealed that the excess remains unchanged over an order of magnitude of Ne partial pressure in the mass spectrometer. This suggests that if the sample stays within this partial pressure range, the excess can simply be corrected out. In the worst-case scenario when the sample is outside of this range, which was not the case for this study, our accuracy could vary by the extent of the excess—thus, by at least ±1%—and would leave the precision unchanged. Intensities of ^{20}Ne (i.e., sensitivity) were found to be variable in the short-term (days/weeks), but long-term (4 months) observation suggests that the variability is natural. ^{20}Ne reproduced by 1.13% (9 outliers out of 103, 1 σ) over this period (Figure 5). We suggest this this should be used as the best representation of the repeatability of a sample. The best two-week period exhibited repeatability that was as low as 0.16% (n = 10), obtained from calibration data acquisition with blank measurements before and after each, with no interruption of the pumping and baking laser pan volume and subsequent sample analysis.
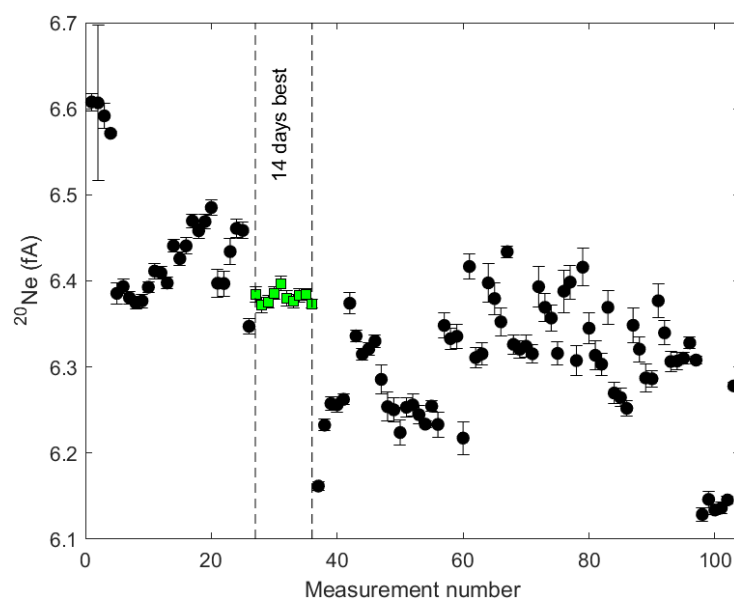
Figure 5. ^{20}Ne intensities from the repeated analysis of 3.2×10^{-11} cm^3 STP ^{20}Ne of air using the ARGUS VI mass spectrometer. Repeatability over the 4 months analytical period was 1.13% (ignoring 9 outliers out of 103). The best 14-day period (green squares) (n = 10) exhibited a repeatability of 0.16% when no interruption of sample analysis occurred. The ^{21}Ne concentration of air/calibration aliquot was equivalent to that of 7.7 mg CREU-1 quartz. Long-term variability seems to be the natural variability of sensitivity, which we think is the best representation of the repeatability of unknowns.

4.2. CREU-1 Quartz

Samples of ~19.9 mg of 250–500 µm CREU-1 quartz [5] were weighed in >99% pure, 20 × 2 mm Pt foil tubes. The tubes were crimped at both ends then placed into 1 cm^2 recesses in a fully degassed Cu pan and pumped to <10^{-8} mbar prior to degassing at 80 °C for 12 h. A sapphire cover glass was used to avoid volatilized metal from adsorbing onto the sapphire viewport. Neon was extracted from the samples by heating to ~1350 °C for 10 min using a 75 W Fusions 970 (Photon Machines) diode laser (970 nm) [23]. Remote operation of the laser was developed during the COVID-related lockdown in late 2020. This, combined with automated gas purification and separation [6], allowed full remote analysis of 10 samples (one laser pan) without the need for laboratory attendance. This significantly increased sample throughput to around 20 samples (2 laser pans) per week and had the advantage that samples could be analysed more closely in time, thereby eliminating slight fluctuations in sensitivity (Figure 5). The cold blanks of the laser pan and the heat of the empty Pt tube (hot blank) were indistinguishable from the system blanks. Isobaric interferences were corrected as above and were similar to air calibrations.

All CREU quartz yielded Ne isotope data plotted on or close to the established spallation line (Figure 6A,B). The ^{21}Ne/^{20}Ne and ^{22}Ne/^{20}Ne ratios varied from 0.00836 ± 0.00007 to 0.01379 ± 0.00022 and from 0.1092 ± 0.00036 to 0.1145 ± 0.00063, respectively. The samples contained higher proportions of air than most samples reported in the international calibration exercise [5,24,25]. This may reflect the low temperature and short duration of the pre-extraction bake out.
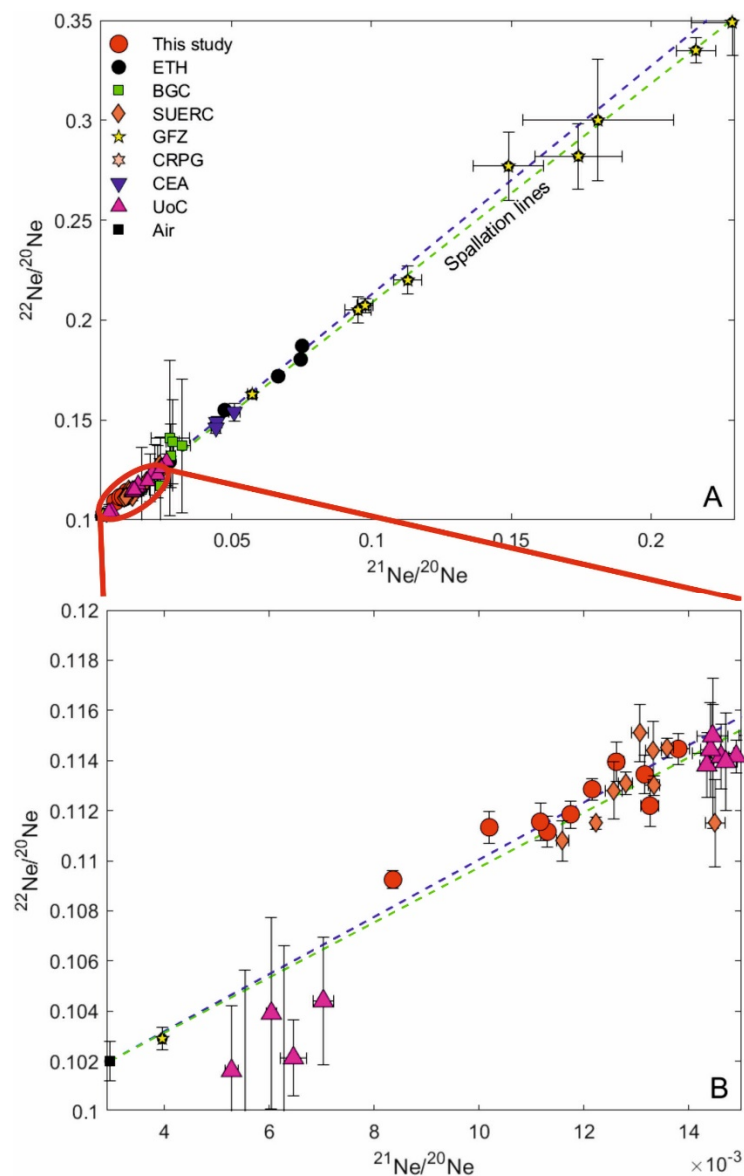
Figure 6. Neon isotope composition of 19.9 mg CREU-1 quartz using the ARGUS VI mass spectrometer. Data were plotted on or close to established cosmogenic spallation lines (**A**) ([26] blue and [27] green), with small deviations that were similar to earlier determinations (**B**). Data were produced over 4 months. Air value (black square) from [6,22]. Other data are from [5,24,25]. ETH (Switzerland), BGC (USA), SUERC (UK), GFZ (Germany), CRPG (France), CEA: China Earthquake Administration (PR China), UoC: University of Cologne (Germany).

The quality of the $^{21}Ne/^{20}Ne$ measurements of CREU quartz, which is the basis for calculating the cosmogenic ^{21}Ne content, is now being assessed against the values obtained in other laboratories. The measurement error is governed by the signal of ^{21}Ne, which is governed by two factors: (1) the degree of cosmogenic compound in the mineral versus atmospheric compound (e.g., how far the sample was located from air on the spallation line) and (2) the mass of the mineral analysed. Consequently, theory would suggest that a higher ^{21}Ne signal (via one of the two factors given above) would lead to a smaller relative error of $^{21}Ne/^{20}Ne$. Unfortunately, when data were plotted on a 3D plot of the relative error of $^{21}Ne/^{20}Ne$ and $^{21}Ne/^{20}Ne$, and the mass of CREU, we were unable to conclude this (Figure 7). We noticed no trend in the error with either increasing mass or $^{21}Ne/^{20}Ne$ and, at this stage, we were unable to compare our performance to that of other laboratories.

We suggest that there is at least one more factor that we have to take into account in order to assess our performance against that of other laboratories.
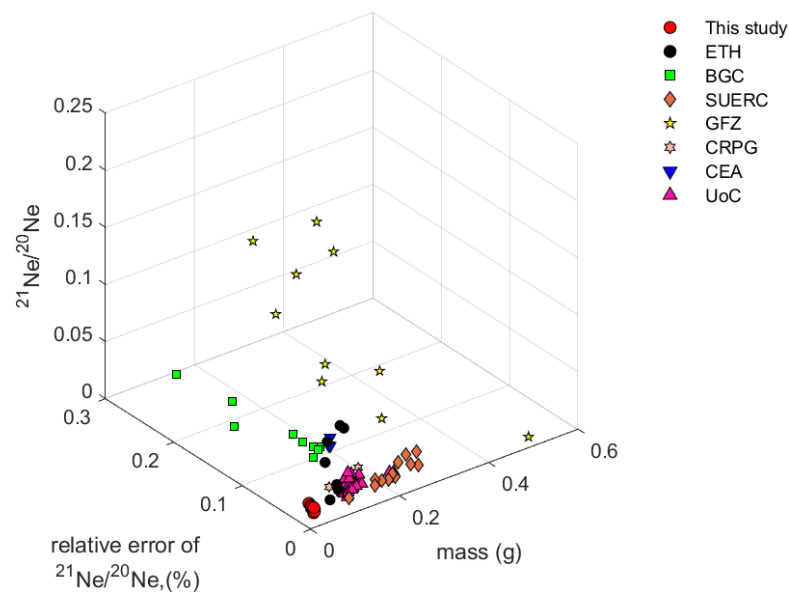
Figure 7. The error of ^{21}Ne/^{20}Ne from CREU-1 quartz with respect to the absolute isotope ratio value and amount of material analysed (mass) from a number of different laboratories. In theory, the relative error (1σ) should decrease with either increasing mass or increasing ^{21}Ne/^{20}Ne or the combination of both. No trend of this nature was observed, suggesting that other factors govern the relative error in the Ne isotope ratio of CREU. ETH (Switzerland), BGC (USA), SUERC (Scotland), GFZ (Germany), CRPG (France): CEA: China Earthquake Administration (PR China), UoC: University of Cologne (Germany). Data are from Refs. [5,24,25].

Using the established procedure [13], the cosmogenic ^{21}Ne content of the CREU-1 quartz samples ranged from 2.91 to 3.73 $\times$ 10^8 atoms/g, with the majority having a much narrower range from 3.08 to 3.50 $\times$ 10^8 atoms/g (Table 2). The mean cosmogenic ^{21}Ne concentration, calculated by fitting the best Gaussian curve (see above), was 3.25 $\pm$ 0.24 $\times$ 10^8 atoms/g (2σ, 2 outliers). While this was 6.6% lower than the accepted value of 3.48 $\pm$ 10 $\times$ 10^8 [5], it overlapped with 2σ. Further, it overlapped with the data from SUERC and GFZ, it was indistinguishable with the data reported by CRPG [5], and the mean value differed from the arithmetic mean to the same extent as the average BGC data (Figure 8). Regarding the outliers, we explain the highest value (3.73 $\times$ 10^8 atoms/g) by a memory effect in the system caused by inadequate pumping due to a failure of the pump for an unknown period of time overnight. The error on ^{21}Ne* was estimated using the 4-month calibration data. As discussed above, we think this is the best representation of instrument performance and avoids underestimation of our error.

These data were obtained from 19.9 $\pm$ 0.5 mg CREU-1 quartz, and constituted, by a significant margin, the smallest amount yet reported (Table 2). Previously published measurements of <250 mg aliquots of CREU-1 quartz [5,24,25] binned in 10 mg groups for each laboratory are plotted in Figure 9. It can be seen that twenty one data groups were produced if we ignore data from the fine fraction from ref. [5] (Table S1). We applied the same statistics as above and ignored groups that would be made up by one data point only. The exception from this is CRPG data, which showed a significant underdispersion.

The cosmogenic ^{21}Ne generated by measurement in early generation static vacuum magnetic-sector mass spectrometers (VG5400 (CRPG, GFZ, CEA) and MAP 215-50 (SUERC)) showed repeatability of between 4% (80 mg) and 2.1% (>200 mg). Data obtained from state-of-the-art analytical systems, e.g., Thermo Fisher ARGUS VI (this study), MAP 215-50 with modern electronics (BGC) and Helix MC Plus (UoC), exhibited a significant

improvement. The data (39 measurements incorporated into 9 groups) appeared to plot along an exponential curve. They implied that modern instrumentation generates a 5-fold improvement in repeatability compared to data produced by VG5400 and MAP 215-50 instruments. This improvement was the result of the combination of several factors. The development of new source electronics led to more stable ion sources. New control software (e.g., Qtegra in the case of the Thermo Fisher mass spectrometers) with built-in regression functions replaced in-house built data manipulation software for old generation mass spectrometers, which resulted in two key outcomes: (1) the generalization of a regression method with improved mathematics and error propagation, and (2) the opportunity for computer-controlled, automatized gas preparation. The latter means more precise reproduction of gas preparation (i.e., opening and closing valves with highly precise time intervals in between steps) and more precise temperature control of cold fingers. We were unable to resolve the question as to which of these factors played the most significant role in improving the repeatability of Ne isotope determinations. The custom-built mass spectrometer at ETH [28] showed the best performance, although one data point was able to fit the exponential model of repeatability and mass of the previous group, but this is not commercially available.

Table 2. Ne data of CREU quartz analysed using SUERC's ARGUS VI mass spectrometer.

Sample	Weight (mg)	^{21}Ne/^{20}Ne	^{22}Ne/^{20}Ne	^{21}Ne*
CREU-A	19.67	0.0084 (1)	0.1092 (4)	332 (6)
CREU-B	19.45	0.0102 (1)	0.1113 (6)	329 (6)
CREU-C	19.36	0.0132 (1)	0.1134 (8)	373 (7)
CREU-D	20.08	0.0122 (1)	0.1129 (4)	350 (7)
CREU-E	20.88	0.0117 (1)	0.1119 (5)	323 (6)
CREU-F	20.29	0.0138 (2)	0.1145 (6)	327 (6)
CREU-G	19.64	0.0133 (2)	0.1122 (8)	308 (6)
CREU-H	19.98	0.0126 (1)	0.1139 (8)	318 (6)
CREU-I	19.18	0.0113 (1)	0.1112 (6)	324 (6)
CREU-J	19.48	0.0112 (1)	0.1116 (7)	291 (5)

1σ errors are shown in parenthesis as last significant figures. ^{21}Ne* is the cosmogenic (non-atmospheric) ^{21}Ne. Concentration is given in cm^3 STP/g $\times$ 10^6, where *p* = 0.101 MPa and T = 0 °C in accordance with [20].
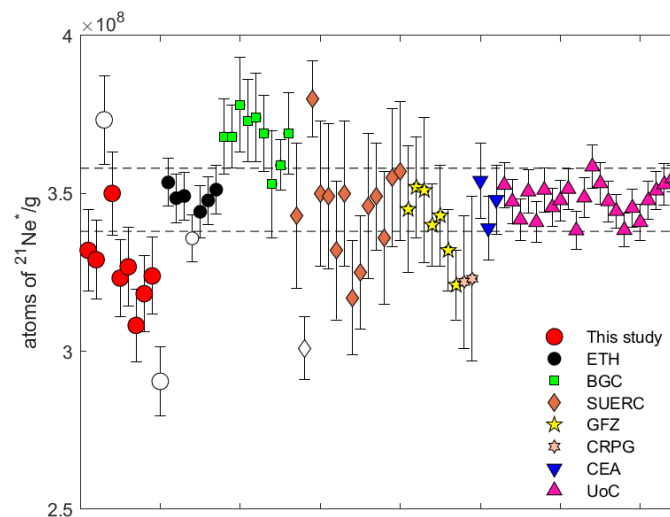
Figure 8. Cosmogenic ^{21}Ne in CREU-1 quartz measured using the ARGUS VI mass spectrometer. Mean value (3.25 ± 0.12 × 10^8 ^{21}Ne* atoms/g, n = 8, 2 outliers) was lower by 6.6% than the accepted standard value (dashed line, 348 ± 10 × 10^8 ^{21}Ne* atoms/g) but it overlapped it within 2σ. Data are after Refs. [5,24,25]. ETH (Switzerland), BGC (USA), SUERC (Scotland), GFZ (Germany), CRPG (France): CEA: China Earthquake Administration (PR China), UoC: University of Cologne (Germany). 2 sigma uncertainties are plotted. Empty: outlier.
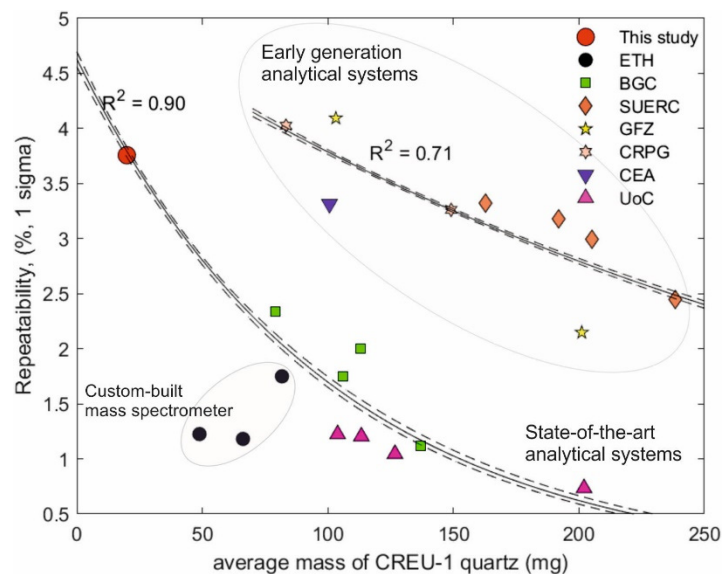
Figure 9. Repeatability of CREU-1 quartz measurements with respect to analysed amounts from a number of different laboratories worldwide. Data from Refs. [5,24,25] were split into groups by masses within 10 mg of material. The only exception was CPRG, which were significantly under dispersed. Data show that beside analysed mass (e.g., signal size of ^{21}Ne) the analytical system is a key factor in data quality. Data from early generation analytical systems (SUERC, CRPG, GFZ, CEA) grouped together and showed the lowest performance at a given mass. Data emerged from state-of-the-art analytical systems including modern electronics, and a high degree of automation (see text) (ARGUS VI in SUERC of this study, BGC and UoC) characterises another group, showing an excellent correlation (n = 9, 39 individual measurements) between the analysed amount of CREU-1 quartz and of ^{21}Ne*. Only the custom-built mass spectrometer (ETH) showed a better performance. We conclude that SUERC's ARGUS VI mass spectrometer analysed 19.9 mg of CREU-1 quartz performs as expected. Apart from three laboratories globally (ETH, BGC and UoC), all laboratories would require the analysis of 5 times or more material to reach the repeatability of this study. ETH (Switzerland), BGC (USA), SUERC (Scotland), GFZ (Germany), CRPG (France): CEA: China Earthquake Administration (PR China), UoC: University of Cologne (Germany). 1 sigma errors on masses are smaller than symbols. Curve errors are 1 sigma.

5. Conclusions and Future Research Directions

The Thermo Fisher ARGUS VI mass spectrometer, tuned for high precision Ne analysis, is now well characterised for the determination of cosmogenic Ne in terrestrial and extra-terrestrial rocks. We characterised the performance in both multi-collection Faraday and peak jumping mode using an electron multiplier. In multi-collection Faraday mode, we replicated the Ne isotope composition of Bruderheim L chondrite and Imilac pallasite. For extra-terrestrial material, we found a 4-fold improvement in the overall uncertainty of the Ne isotope ratio (0.5%) compared to that obtained using 2–6 times more material in earlier works. We suggest that a 5–10-fold reduction in the repeatability may be obtained, albeit more measurement would be needed to confirm this. Peak jumping on the CDD detector allowed the analysis of cosmogenic Ne in ~19.9 mg CREU-1 quartz, which was 3–5 times less than ever reported in previous studies and the acquisition of calibration data at the level of $9.36 \pm 0.21 \times 10^{-14}$ cm^3 STP ^{21}Ne (equivalent of 7.7 mg CREU). We reproduced ^{21}Ne/^{20}Ne with 1.1% (1σ) (n = 103), which was a significant achievement at this Ne partial pressure. Our CREU measurement yielded to ^{21}Ne* content of $325 \pm 12 \times 10^6$ ^{21}Ne* atoms/g (n = 8), which overlaps with the internationally accepted value within 2σ. The reproducibility of ^{21}Ne* (3.7%, 1 sigma) was exactly what the relationship of repeatability and sample mass would suggest, established by data obtained from similar, state-of-the-art analytical systems. This was a ~4 times improvement in comparison to early generation

analytical systems. The remote operation of laser heating and the automation of gas purification, separation and analysis procedures increased sample throughput and exact repetition of the procedure and, by allowing more calibration and blank measurements, would likely produce better quality data. The ability to determine Ne isotopes in small amounts of material will be invaluable in studies where sample material is extremely limited, e.g., planetary and comet return missions, and when the appropriate mineral phase is in low abundances in terrestrial or extra-terrestrial rocks.

The incorporation of high gain Faraday amplifiers (10^{13} Ohm and beyond) may allow further improvements in data quality and reductions in sample size for the analysis of cosmogenic Ne-rich material. However, ^{21}Ne analysis from terrestrial samples will likely remain beyond the reach of Faraday detectors with existing amplifier technology and mass spectrometer sensitivity. For small sample analysis, effort will focus on reducing the background level of CO_2, which will prove difficult to resolve without the application of high-resolution instrumentation, e.g., that of [29], and the exploration of the advantages of multi-collection using combined CDD–Faraday.

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