und WÄNKE[13] für die von Beardsley (20,6 ± 1,1) Zerfälle/min · kg. In einem Targetexperiment schließlich bombardierten STOENNER, SCHAEFFER und DAVIS[4] u. a. Ca und K hinter 10 cm Stahl mit 3 BeV-Protonen und fanden offensichtlich für das Verhältnis $P_{\text{Ca}}(^{39}\text{Ar})/P_{\text{Fe}}(^{39}\text{Ar}) \approx 1{,}4$. (Der Wert selbst ist in der Arbeit nicht angegeben, er wurde aus den Daten der Tab. 2 dieser Autoren berechnet.) Die große Diskrepanz ist wohl kaum auf Meßfehler zurückzuführen. Der niedere Wert des Targetexperimentes deutet vielmehr auf einen wesentlich geringeren Flux von schnellen sekundären Neutronen hin und zeigt, daß große Änderungen des Verhältnisses zu erwarten sind.

Zur weiteren experimentellen Prüfung sind Messungen der hier beschriebenen Art an einigen der extrem verschiedenen Meteoriten der Tab. 4 geplant.

Für ihre Hilfe bei den experimentellen Arbeiten danken wir Frl. U. SCHEERER und Frl. U. KREBS. Die Arbeit wurde finanziell durch das Bundesministerium für Atomkernenergie und Wasserwirtschaft unterstützt.

The Isotopic Composition of Atmospheric Neon *

J. R. WALTON and A. E. CAMERON

Oak Ridge National Laboratory, Oak Ridge, Tennessee

(Z. Naturforschg. **21 a**, 115—119 [1966]; received 17 September 1965)

Dedicated to Prof. J. MATTAUCH *on his 70th birthday*

"Absolute" values for the isotopic abundance ratios of atmospheric neon have been determined by mass spectrometry. Calibration standards were prepared by mixing of nearly pure separated nuclides of neon. The percentage abundance of the three nuclides of neon are:

$$^{20}\text{Ne} = 90.514 \pm 0.031, \quad ^{21}\text{Ne} = 0.266 \pm 0.005, \quad ^{22}\text{Ne} = 9.220 \pm 0.029.$$

The calculated atomic weight of neon on the unified physical and chemical atomic weight scale ($^{12}\text{C} = 12$) is 20.1794 ± 0.0030.

The reinvestigation of the isotopic composition of atmospheric neon reported here was undertaken for several reasons. The mass spectrometric measurements in the recent literature [1–3] were not in good agreement. It was not clear whether the lack of agreement might be ascribed to difference in the mass discrimination in the different instruments with which the measurements were made or whether, because of the relatively large percentile mass difference between ^{20}Ne and ^{22}Ne, there could have been isotopic fractionation in the course of the commercial recovery of neon from the atmosphere. In the neon isotopic abundance measurement reported by NIER[1], the mass spectrometer was calibrated for mass discrimination by measurement on the doubly charged ions of an argon standard which had been prepared by mixing ^{36}Ar and ^{40}Ar of high isotopic purity from a thermal diffusion separation.

The atomic weight of neon in the complete revision of the "Table of Relative Atomic Weights" issued in 1961, when the physical and chemical atomic mass scales were unified on the basis of $^{12}\text{C} = 12$, was still based upon gas density measurements made by BAXTER and STARKWEATHER in 1928[4]. This number could be verified for accuracy if reliable isotopic abundance figures were available. In addition, there is potential geochemical interest in the reactions $^{18}\text{O}(\alpha, n)\,^{21}\text{Ne}$ and $^{19}\text{F}(\alpha, n)\,^{22}\text{Ne}$. Indeed, a result of these reactions appears to have been observed in neon recovered from helium-bearing natural gases[5]. A reliable and reproducible reference sample would be highly desirable and atmospheric neon, if invarient in isotopic composition as obtained, could fulfill this need.

Samples of ^{20}Ne and ^{22}Ne were available in high chemical and isotopic purity as a result of a thermal

---

* Research sponsored by the U.S. Atomic Energy Commission under contract with the Union Carbide Corporation.

[1] A. O. NIER, Phys. Rev. **79**, 450 [1950].

[2] V. H. DIBELER, F. L. MOHLER, and R. M. REESE, J. Res. Nat. Bur. Stand. **38**, 617 [1947].

[3] R. F. HIBBS, Mass Spectrometric Measurements of Natural Isotopic Spectra, Report No. AECU-556 [1949].

[4] G. P. BAXTER, J. Amer. Chem. Soc. **50**, 603 [1928]. — G. P. BAXTER and H. W. STARKWEATHER, Proc. Nat. Acad. Sci. US **14**, 50 [1928].

[5] "The Isotopic Abundance of Neon from Helium-Bearing Natural Gases", D. E. EMERSON, L. STROUD, and T. O. MEYER, Bureau of Mines, Amarillo, Texas, submitted to Geochim. Cosmochim. Acta.

diffusion operation in the Isotopes Division of the Oak Ridge National Laboratory. The quantities of the separated isotopes were adequate to make possible the quantitative preparation of synthetic mixtures of the two major neon isotopes with which the overall bias of the mass spectrometer could be determined and corrected for.

Mass Spectrometry

A 15 cm radius, 60° deflection mass spectrometer was used in the measurements. Ionization was by 65 volt electrons. The accelerating voltage was fixed at 2 kv. The current was measured by an Applied Physics Corporation vibrating reed electrometer with a 10^{10} Ω input resistor and recorded with a Brown strip chart recorder. A single collector was used. Mass spectra were scanned magnetically, first in one direction and then in the other to minimize the effect of drift.

The gas leak into the ionization chamber was a one mil hole in a one mil gold sheet. A calibration study of the leak indicated that the gas flow was molecular. No measurable change in the composition of the gas in the ionization region was found during the short time of analysis. The volume back of the leak was 1475 ml. The pressure in this volume during measurements was approximately 0.1 Torr.

Isotopic Standards

The Isotopes Division at Oak Ridge National Laboratory had available ^{20}Ne and ^{22}Ne with isotopic purity greater than 99 per cent. The separated isotopes were produced by thermal diffusion. Residual impurities were determined on the mass spectrometer and were principally nitrogen, water and hydrogen.

An apparatus for volumetric mixing of the separated isotopes to make standards of known isotopic composition is shown in Fig. 1. The apparatus consisted of three bulbs connected by capillary tubing. The volumes, including the bore of the upper stopcock, marked 6 in the Figure, to etched lines on the capillary tubing below each bulb were determined by filling with mercury and weighing. The three known volumes were: 15.077; 34.778; and 50.493 ml at 22 °C. The accuracy of the volume measurements was dependent upon the accuracy of the weighing balance which was ±0.0005 gm.

The separated isotopes from which the standards were mixed were attached at "A" and "B". The mixed standard was collected in flask "C". Unused standards components were collected in "D" by the Toepler pump. Pressures were determined by reading the large bore manometer with a cathetometer, making appropriate temperature corrections. The cathetometer was read to ±0.005 mm. During the standard mixings the temperature was held as constant as could be arranged. The temperature was known to better than 0.1 °C. The error in mixing of the gas standards composed of errors in volume, pressure and temperature was less than 0.05 per cent.

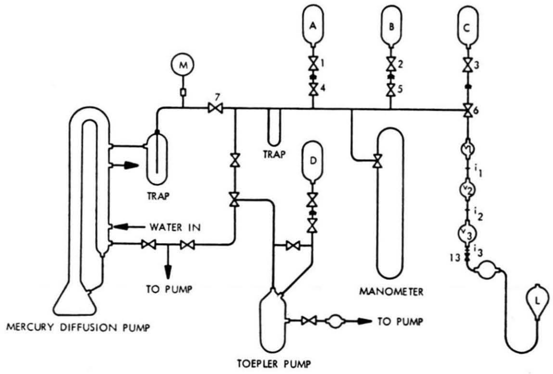

Fig. 1. Apparatus for preparing standard gas mixtures.

Standard No.	Volume	Pressure cm Hg	Temp. °K	Gas	Composition (Atom Per Cent)			Impurities
					^{20}Ne	^{21}Ne	^{22}Ne	
1	49.855	7.347	297.25	^{20}Ne	99.830	< 0.005	< 0.005	0.160
	15.077	2.377	297.25	^{22}Ne	0.021	0.034	99.596	0.349
3	49.855	6.043	296.75	^{20}Ne	99.830	< 0.005	< 0.005	0.160
	15.077	2.058	296.75	^{22}Ne	0.021	0.034	99.596	0.349
4	49.855	4.867	297.70	^{20}Ne	99.830	< 0.005	< 0.005	0.160
	15.077	4.270	297.50	^{22}Ne	0.021	0.034	99.596	0.349
5	49.855	2.455	299.00	^{20}Ne	99.771	< 0.005	< 0.005	0.220
	49.855	2.368	299.00	^{22}Ne	0.026	0.032	99.534	0.408
6	15.077	1.640	299.75	^{20}Ne	99.771	< 0.005	< 0.005	0.220
	49.855	1.637	299.80	^{22}Ne	0.026	0.032	99.534	0.408

Table 1. Composition of Isotopic Standards.

Six standards were mixed but one had to be rejected because of an obvious error in recording of data. The remaining five standards are tabulated in Table 1, which gives the volume, pressure, temperature and the composition of the separated isotopes determined at the time of mixing.

Any contamination, both isotopic and chemical, that occurred during repeated handling of the starting materials was determined and corrections were made.

The results of the measurements of the five standards are given in Table 2.

Standard No.	Calculated	Measured	Calculated / Measured
1	9766	9644	1.0127
3	10281	10146	1.0133
4	26491	26349	1.0054
5	96208	95770	1.0046
6	329202	328552	1.0020

Table 2. $^{22}Ne/^{20}Ne$ (× 10^5) Ratios for Neon Standards.

The ratio $^{22}Ne/^{20}Ne$ ($\times 10^5$) is tabulated for the calculations from the data in Table 1, and for the mass spectrometer results. The ratio of ratios, calculated/measured, is given in the last column. This is the quantity by which the determined ratio must be multiplied to give the true ratio in the standards. The "bias" in the mass spectrometer is readily seen to be a function of the composition. This is shown graphically in Fig. 2 where the ratio of ratios is plotted as a function of the ^{20}Ne concentration. The line drawn is the calculated least squares fit, assuming that the bias is linear with concentration of ^{20}Ne. This assumption is not necessarily correct, and the position of the points would make it appear that it is non-linear.

For the purpose of this investigation, the bias was determined at the natural isotopic composition from the two standards which bracketed the atmospheric composition, Standards 1 and 3. The ratio of ratios used was 1.0130 ± 0.0044.

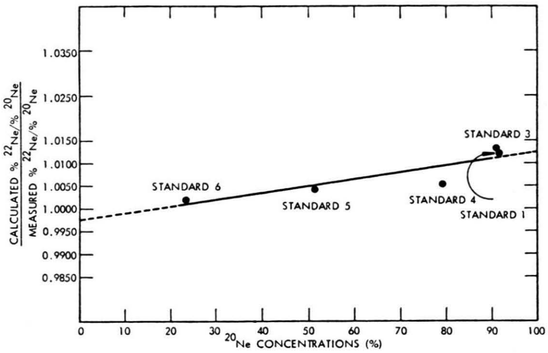

Fig. 2. Mass spectrometer bias as a function of ^{20}Ne concentration.

In all measurements of neon standards and samples, the mass 40 and 44 positions were monitored to insure that no significant contribution from $^{40}Ar^{++}$ and CO_2^{++} occurred at the neon masses. No other gas samples were introduced into the instrument during the series of neon measurements.

Atmospheric Neon

The six samples of neon gas recovered from the atmosphere and obtained from commercial suppliers were run on the mass spectrometer alternately with a standard. The measurement series was completed with the standard. The results of the measurements are tabulated in Table 3.

The two samples of neon supplied by the Linde Company were located in the laboratory. The identifying numbers were different and they were presumably produced at different times. The sample identified as NBS-101 was obtained from the National Bureau of Standards. This is a "comparison standard" which

Sample	Measured $\frac{^{21}Ne}{^{20}Ne}$ ($\times 10^5$)	Recalculated $\frac{^{21}Ne}{^{20}Ne}$ ($\times 10^5$)	Measured $\frac{^{22}Ne}{^{20}Ne}$ ($\times 10^5$)	Recalculated $\frac{^{22}Ne}{^{20}Ne}$ ($\times 10^5$)
Linde 6289	293.3 ± 6.2	295.2 ± 6.2	10035 ± 35	10165 ± 35
Linde 456194	291.4 ± 4.2	293.3 ± 4.2	10070 ± 27	10200 ± 27
NBS 101	293.3 ± 4.5	295.2 ± 4.5	10024 ± 39	10154 ± 39
Airco F0626110	288.9 ± 7.9	290.8 ± 7.9	10077 ± 28	10208 ± 28
Airco F1116114	293.8 ± 5.2	295.7 ± 5.2	10091 ± 43	10222 ± 43
Airco E1214050	288.9 ± 7.2	290.8 ± 7.2	10041 ± 58	10172 ± 58
	Average	293.5 ± 5.8		10187 ± 38

Table 3. Isotopic Ratios.

is available on request to interested mass spectrometer users. It is not considered a standard in the usual sense, but can insure that different workers have identical material upon which to make measurements. The three Airco samples were obtained in one liter flasks from Air Reduction Company at Bound Brook, New Jersey, through the kindness of A. T. Barsocchi. These were different batches of neon separated at different times over an 18-month period. The results of measurements on these samples are tabulated in Table 4 and will be discussed below.

Within the limits of the measurements and for this suite of samples, there is no significant difference. This would indicate that the process of recovery of this gas from air does not introduce a variation of any significance in isotopic composition. The columns headed "recalculated" are the isotopic ratios observed in the atmospheric neon samples corrected by use of the "bias" correction of 1.0130 ± 0.0044. For correction of the $^{21}\text{Ne}/^{20}\text{Ne}$ ratio the assumption was made that from masses 20 to 22, the bias was linear.

Atomic Weight of Neon

From the corrected ratios the percentage composition of neon is determined and shown in Table 4.

Nuclides	Per Cent
^{20}Ne	90.514 ± 0.031
^{21}Ne	0.266 ± 0.005
^{22}Ne	9.220 ± 0.029

Table 4. Isotopic Abundance of Neon.

The atomic weight of neon, as published in the 1961 revision of the Table of Atomic Weights, is 20.183. This was based upon gas density measurements made by Baxter and Starkweather [4], and by Baxter [4] in 1928. The value was recalculated by Professor T. Batuecas, then President of the International Commission on Atomic Weights. The Table was published upon the basis of $^{12}\text{C} = 12.0$.

The atomic weight is calculated by multiplying the fractional compositions of the three isotopes by the atomic masses.

Nuclides	Atomic Percent	Atom Mass
^{20}Ne	90.514 ± 0.031	19.99244
^{21}Ne	0.266 ± 0.005	20.99385
^{22}Ne	9.220 ± 0.029	21.99138
	Calculated Atomic Weight	20.1794 ± 0.0030
	1961 Atomic Weight Table	20.183

Table 5. The Atomic Weight of Neon ($^{12}\text{C}=12$).

The atomic masses are taken from the compilation of König, Mattauch and Wapstra [6]. The value in the Table of 20.183 is stated without error limits, but these would undoubtedly overlap the mass spectrometer results. The agreement is excellent.

The uncertainties in the atomic weight calculations are shown in Table 6.

Ratio Determinations	± 0.00042
Gas Composition of Neon Standards	± 0.0006
Nuclidic Masses	± 0.0000019
Gas Mixing	± 0.0020
Total	± 0.0030219

Table 6. Uncertainties in the Atomic Weight Calculations of Neon.

Discussion

The measurements reported above had been completed when we learned of the work of Eberhardt, Eugster and Marti on the same subject [7]. They recovered neon from air by a process which could introduce no isotopic fractionation and measured its isotopic composition. They prepared one isotopic standard by mixing known amounts of atmospheric neon with 99.7% ^{22}Ne. Their mass spectrometer was calibrated with this standard. They found that a neon sample from a commercial source of this gas agreed in isotopic composition with those which they

	^{20}Ne	^{21}Ne	^{22}Ne
This Work	90.514 ± 0.031	0.266 ± 0.005	9.220 ± 0.029
Eberhardt, Eugster and Marti[7]	90.50 ± 0.07	0.268 ± 0.002	9.23 ± 0.07
Nier	90.92 ± 0.04	0.257 ± 0.001	8.82 ± 0.04

Table 7. Isotopic Composition of Neon, Atom Per Cent.

---

[6] L. A. König, J. H. E. Mattauch, and A. H. Wapstra, Nucl. Phys. **31**, 18 [1962].

[7] P. Eberhardt, O. Eugster, and K. Marti, Z. Naturforschg. **20 a**, 623 [1965].

had themselves recovered from the atmosphere. This indicates, as we have shown above, that the neon gas from commercial sources seems not to have undergone any isotopic fractionation.

The agreement between the measurements of Eberhardt, Eugster and Marti and the results which we report here is very gratifying. The isotopic compositions from the two pieces of work are tabulated below, together with the results of Nier's measurements.

It is difficult to see why the measurements of Nier, calibrated as they were against $^{36}Ar^{++}$ and $^{40}Ar^{++}$ from a synthetic standard appear to be so much in error. He found it necessary to correct for the residual mass 18 peak from water vapor in the instrument, but verified his correction by introducing isotopically pure ^{40}Ar to ascertain whether the mass 18 peak increased when argon was admitted. No explanation is readily proposed for the fact that the mass 20 peak observed in his neon measurements was too great.

The atomic weight of neon calculated from the first and second abundance in the above table is 20.179 with an error of ±0.003 for our work and an error of ±0.002 quoted by Eberhardt, Eugster and Marti.

K-Ar-Altersbestimmungen an Ultrabasiten des Baltischen Schildes

T. Kirsten und W. Gentner

Max-Planck-Institut für Kernphysik, Heidelberg

(Z. Naturforschg. 21 a, 119—126 [1966]; eingegangen am 5. Oktober 1965)

Herrn Professor J. Mattauch *zum 70. Geburtstag gewidmet*

The K-Ar-ages of five ultrabasic rocks from the Baltic Shield were determined. K-Ar-ages of 3.7 to 8.8×10^9 y were obtained. Two samples were cut into fractions with different potassium content and a partial correlation of the argon content with the potassium content in the separated fractions was noticed. The question of extraneous argon causing higher age values is discussed. Taking into consideration the previous results obtained by Gerling et al., it may be said, that extremely high Ar^{40}/K-ratios are the rule for ultrabasic rocks from the Baltic Shield. As a consequence of this fact, it is not likely that all these rocks have the age only of the precambrian pluton in which they are incorporated. Assuming that the alpinotype peridotites were transported upwards in the form of solid fractions from the upper mantle, it is possible, that actually radiogenic argon exists more or less in the sample.

The highest Ar^{40}/K-ratios (according to ages ranging from 5.9 to 10.9×10^9 y) exhibit the samples with potassium contents below 100 ppm. Samples with potassium contents more than 1‰ have much smaller Ar^{40}/K-ratios (according to ages from 4.2 to 5×10^9 y). Excess argon probably causes the extremely high "ages" of more than 7×10^9 y. The ages from relative potassium-rich samples will eventuible show the true age. The most likely value for this age is 4.2×10^9 y, measured for a peridotite with 0.49% potassium content.

Neuerdings sind die irdischen Ultrabasite ein bevorzugter Gegenstand isotopengeochemischer Untersuchungen [1–9]. Man hofft hierdurch unser Wissen über den oberen Erdmantel zu erweitern.

Die gegenwärtige Kenntnis der Zustände und Prozesse, die im Mantel eine Rolle spielen, wie Aggregatzustand, stoffliche Zusammensetzung, Differentiationsprozesse, Druck- und Temperaturverhältnisse

---

[1] E. K. Gerling, J. A. Shukoljukov, I. I. Matvejeva, T. V. Koltsova u. S. S. Jakovljeva, Geokhimiya **1962**, 11.

[2] E. K. Gerling u. J. A. Shukoljukov, Geokhimiya **1963**, 4, 365.

[3] E. K. Gerling, W. A. Maslenikov, I. M. Morossova, I. I. Matvejeva u. S. N. Wasiljeva, Das absolute Alter präkambrischer Gesteine der Sowjetunion (russisch), Akademie der Wissenschaften der UdSSR, Moskau 1965, p. 11.

[4] E. K. Gerling, W. A. Maslenikov u. I. M. Morossova, XXth IUPAC, Moscow 1965, paper C 43.

[5] I. McDougall u. D. H. Green, Norsk Geol. Tidsskr. **44**, 183 [1964].

[6] J. F. Lovering u. J. R. Richards, J. Geophys. Res. **69**, 4895 [1964].

[7] G. D. Roe, W. H. Pinson u. P. M. Hurley, Abstracts from 46. Meeting of AGU (1965). — G. D. Roe, Bericht MIT 1381-12, 159 [1964].

[8] A. M. Stueber u. V. R. Murthy, Abstracts from 46. Meeting of AGU [1965].

[9] L. T. Aldrich, S. R. Hart, G. R. Tilton, G. L. Davis, S. N. Rama, R. Steiger, J. R. Richards u. J. S. Gerken, Annual report of the director of the department of terrestrial magnetism, Carnegie Institution, Washington 1964, p. 330.