Absolute Isotopic Abundance Ratios and Atomic Weight of a Reference Sample of Strontium

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Absolute values have been obtained for the isotopic abundance ratios of a reference sample of strontium using solid sample thermal ionization mass spectrometry. Samples of independently known isotopic composition prepared from chemically pure and nearly isotopically pure separated strontium isotopes were used to calibrate the mass spectrometry. The resulting absolute $^{88}Sr/^{86}Sr$, $^{87}Sr/^{86}Sr$, and $^{84}Sr/^{86}Sr$ ratios are 8.3786 ± 0.0033, 0.71034 ± 0.00026, and 0.05655 ± 0.00014 respectively which yields atom percents of: ^{88}Sr = 82.5845 ± 0.0066, ^{87}Sr = 7.0015 ± 0.0026, ^{86}Sr = 9.8566 ± 0.0034, and ^{84}Sr = 0.5574 ± 0.0015. The atomic weight calculated from these abundances is 87.61681 ± 0.00012. The indicated uncertainties are overall limits of error based on 95 percent confidence limits for the mean and allowances for the effects of possible systematic error.

Key Words: Absolute ratios; atomic weight; isotopic abundances; strontium.

1. Introduction

The analytical mass spectrometry group of the National Bureau of Standards is conducting a long term program of absolute abundance ratio and atomic weight determinations on polynuclidic elements using predominantly thermal ionization mass spectrometry though, on occasion, electron impact ionization has been used. Previous elements studied include silver [1],[1] chlorine [2], copper [3], bromine [4], chromium [5], magnesium [6], lead [7], boron [8], rubidium [9], rhenium [10], silicon [11], potassium [12], and thallium [13]. The present work extends the study to strontium.

Natural strontium consists of four isotopes, ^{88}Sr, ^{87}Sr, ^{86}Sr, and ^{84}Sr. One of these, ^{87}Sr, is constantly, though slowly, accumulating as the end product of the decay of ^{87}Rb; the other three are believed to be of stable abundance.

The present atomic weight of strontium, 87.62, is based on the relative isotopic measurements of A. O. Nier [14] on a piece of pure strontium metal. Since this early work there has been no serious effort focused toward the determination of the absolute isotopic abundances of strontium. In the interim, the value of 0.1194 determined by Nier for the ratio $^{86}Sr/^{88}Sr$ has been nearly universally adopted by the geological community as an interlaboratory standardization value in the mass spectrometric measurement of radiogenic ^{87}Sr.

The large limit of error (± 2 percent) associated with Nier's measurement of $^{86}Sr/^{88}Sr$ left some uncertainty about a possible systematic error associated with the currently accepted procedure of correcting for instrumental fractionation of the isotopes by normalizing to Nier's $^{86}Sr/^{88}Sr$ ratio (= 0.1194). Thus, one primary purpose for the present work was to provide absolute values for the strontium isotopic ratios which might be used as a reference for the hundreds of papers published annually dealing with strontium isotope geology and geochronology.

In the present study the mass spectrometers were calibrated for bias by the use of samples of independently known $^{88}Sr/^{86}Sr$ ratios, prepared from chemically pure and nearly isotopically pure ^{88}Sr and ^{86}Sr solutions. These measured biases were then used to correct the raw data obtained on a reference sample of strontium thus yielding absolute values for this sample. The reference sample selected for this work was SRM 987, Strontium Carbonate, which is a highly purified material previously certified for strontium content.

2. Experimental Procedure

2.1. Mass Spectrometry

Isotopic measurements were performed using a triple filament rhenium ion source. The ionizing filaments used in the measurements were rigorously degassed at 5 A (>2000 °C) for 2 h to reduce any background ion contributions to the $^{86,87,88}Sr$ mass positions to <0.01 percent of the ion beam intensities used in the measurements of the "natural" strontium, SRM 987. The viability of this procedure was supported by scanning these mass positions while heating a "blank" ionizing filament at temperatures in excess of the usual operating temperature (1600 °C). Any possible contribution to these masses under actual analysis conditions was evaluated

by determining the absence of minor isotope perturbations in the analyses of SRM 988, [84]Sr spike, which has [86]Sr, [87]Sr, and [88]Sr atom fractions of 0.00059 ± 0.00001, 0.00010 ± 0.00001, and 0.00039 ± 0.00001, respectively [15]. Using this technique, any contribution to the [85]Rb mass position was observed to be $<10^{-15}$ A, and a factor of 2.6 less for the [87]Rb based on a natural [85]Rb/[87]Rb ratio of 2.59 [9].

Details of the strontium isotopic analysis technique have been published [16]. Generally, the procedure consists of adding a drop of solution [500 μg Sr/mL in 2% (V/V)HNO$_3$] to each of two degassed 0.001 inch × 0.030 inch regular rhenium filaments, drying under an infrared lamp and heating the resulting deposit with sequentially higher alternating currents to a final dull red heat. In the latter step the deposit "collapses" on the filament and undergoes an apparent reaction with the rhenium filament material to form a compound probably analogous to the $Ca_3Re_2O_9$ and $CaReO_4$ detected by electron diffraction earlier during Ca analyses [17].

This technique has been used extensively in this laboratory for hundreds of strontium analyses, and has been adopted by several geological laboratories around the world. Experience has shown that inter-analysis variations in the unnormalized [86]Sr/[88]Sr ratio can be held to <0.05 percent, relative, and usually substantially better using rigidly controlled analysis parameters.

The two spectrometers used in these measurements were nominally identical 90° sector, 30 cm radius of curvature instruments equipped with thin lens Z-focusing ion sources and a conventional NBS-designed collector appropriately biased and baffled to minimize problems due to secondary particles [18]. Both measuring systems used Cary 401 MR^2 vibrating reed electrometers whose attenuator resistors and amplifier linearities were calibrated relative to each other within ± 0.01 percent by placing precisely known relative voltages into the feedback loop of the electrometer. The 1 V analog output of the electrometer was digitized using two different systems: the instrument of operator I used a Hewlett-Packard 2212B voltage-to-frequency convertor (full scale = 100 kHz) coupled to a high speed ATEC scaler; operator II's instrument used a Teledyne (4501A) voltage-to-frequency convertor unit in tandem with a high speed scaler of NBS design. Data acquisition and instrument control for both instruments were achieved with Hewlett-Packard 9830A(B) programmable calculators, using software developed in this laboratory. In the absence of a priority interrupt capability for the calculator, the software was arranged such that the data averaging and printing segment at the end of each peak top measurement was completed in time for the calculator to be ready for the next data transmission sequence from the scaler-VFC unit.

In the process of thermally vaporizing and ionizing samples, a mass dependent isotopic discrimination occurs that produces an observed isotope ratio that is not characteristic of the sample. This discrimination occurs among sample loadings and during a sample analysis. To minimize any discrimination-induced skewing of the relative isotope ratios with respect to a common time base during an analysis, the isotope ratios were measured symmetrically with respect to mass. Typically, each peak was monitored for 10 precisely timed 1 s integrations, and 8–10 s (30–60 s for the separated isotope mixtures) were allowed between signal integration periods to allow for the RC decay of the electrometer as well as for a settling time for the magnetic field. Normally 10 to 20 ratios were measured for each isotope per analysis.

2.2. Purification of the Separated Isotopes

To prepare accurate isotopic standards for strontium, it is necessary to know, as accurately as possible, the concentration of strontium in solutions of separated isotopes of strontium. To accomplish this objective a purification method and an assay procedure were developed that enabled us to determine the concentration of strontium in a solution with an accuracy of ±0.01 percent.

Electromagnetically separated [86]Sr and [88]Sr isotopes in the form of strontium nitrate were obtained from the Nuclear Division of the Oak Ridge National Laboratory. The $^{86}Sr(NO_3)_2$ was designated series 136801 and the $^{88}Sr(NO_3)_2$ was designated series 137001. The certificates of analysis which accompanied each sample included a semi-quantitative spectrographic analysis which showed that several impurity elements could be present at the 0.02 to 0.05 percent level.

To reduce those impurities to a level low enough so that they could not cause a significant error in the assay of strontium, the separated isotope samples were further purified. The purification procedure used was based on the relative insolubility of strontium nitrate in concentrated nitric acid. Only two elements, barium and lead, are known to co-precipitate under this condition [19]. If a dilute nitric acid solution is evaporated, the nitric acid concentration increases until the azeotropic solution containing 68 percent HNO$_3$ is reached [20]. In 68 percent HNO$_3$ the solubility of strontium nitrate is almost zero [21] while the solubility of most cations except barium and lead is sufficient to keep them in solution [19]. Lead can be efficiently removed by anodic electrodeposition but barium is not separated and remains as an impurity in the strontium nitrate.

The effectiveness of the purification procedure described below was first tested by the purification of natural strontium nitrate which had been doped with 1000 ppm each of 30 common impurity elements.

The results of the analysis of this material by spark source and thermal isotope dilution mass spectrometry are shown in

table 1. The methods of analysis are also described below. Only sodium was detected at a concentration greater than 1 $\mu g/g$ while all of the other elements were at the sub-ppm level. Barium was not determined since the purification method would not remove it and a correction for its concentration in each separated isotope is necessary.

Each strontium separated isotope was purified as follows: The strontium nitrate, $Sr(NO_3)_2$, (about 5.0 g) was transferred to a 100 mL Teflon-FEP beaker and dissolved in 50 mL of water. One mL of 1 mol/L hydrochloric acid was added and the solution was heated at about 90 °C on a hot plate for two hours. The solution was filtered through a close-textured filter paper into a Teflon-FEP beaker. Five mL of high-purity nitric acid was added to the filtrate and the solution was heated to about 90 °C on a hot plate. Strontium nitrate was crystallized by allowing the solution to evaporate until only about 3 mL of solution remained (68% HNO_3). The beaker and contents were allowed to cool to room temperature. The solution was

withdrawn from the crystals of strontium nitrate by using a plastic hypodermic syringe with a platinum needle. The crystals were washed twice with 1 mL portions of nitric acid which were withdrawn in the same manner. The excess nitric acid was then removed by heating the beaker until the crystals were dry.

Lead was removed from the crystallized strontium nitrate by dissolving it in about 50 mL of water and electrodepositing overnight onto platinum wire electrodes at an applied voltage of 2.0 V. Under those conditions, lead will deposit as PbO_2 onto the anode.

Only a slight deposit (<5 μg Pb) was noted on the anode from the "Sr 86" solution but there was a heavy deposit on the anode from the "Sr 88" solution with considerable PbO_2 on the bottom of the beaker. The "Sr 88" solution was filtered thru acid washed close-textured filter paper. After the addition of 5 mL of nitric acid to each solution, strontium nitrate was recrystallized as described above and lead was removed by electrodeposition in the same manner. Only a faint deposit (about 1 μg) was noted on the anode from the "Sr 86" solution but once again the deposit on the anode from the "Sr 88" was heavy and particles of PbO_2 were on the bottom of the beaker, necessitating filtration of the solution.

The cycle of crystallization and electrodeposition was repeated four times for the "Sr 88" solution until the anode showed no evidence of PbO_2 after electrodeposition. (The total amount of lead from the "Sr 88" solution amounted to 0.1% of the starting weight of $^{88}Sr(NO_3)_2$.)

The final solutions from the lead separations were evaporated to dryness and the salts were transferred to two platinum crucibles, dried, and weighed. Calculations based on the starting weights of $^{86}Sr(NO_3)_2$ and $^{88}Sr(NO_3)_2$ and the weights of the corresponding purified salt showed that about 99 percent of the strontium was recovered in each case.

The acids and water used in those purifications were produced at NBS by sub-boiling distillation [22] and have been shown to be extremely low in trace cation contamination. Apparatus such as beakers and filters were cleaned with high-purity acid before use.

2.3. Analysis of Purified Strontium Separated Isotopes

About 0.5g samples of each purified strontium isotope as $Sr(NO_3)_2$ were dissolved in 10 mL of water in a Teflon beaker and spiked with 10^{-7}g of ^{109}Ag, ^{111}Cd, ^{142}Ce, ^{53}Cr, ^{65}Cu, ^{54}Fe, ^{71}Ga, ^{113}In, ^{26}Mg, ^{97}Mo, ^{145}Nd, ^{62}Ni, ^{82}Se, ^{117}Sn, ^{125}Te, ^{47}Ti, ^{203}Tl, ^{67}Zn, and ^{91}Zr. Each solution was treated as follows: 1 mL of nitric acid was added and the solution was evaporated until most of the strontium crystallized and about 0.5 mL of nitric acid remained. The nitric acid was removed from the crystallized strontium nitrate with a polypropylene hypodermic syringe equipped with a platinum needle and transferred to a Teflon beaker. The crystals of $Sr(NO_3)_2$ were

TABLE 1. *Analysis of Purified Strontium*

Element	Spike Isotope	Natural $Sr(NO_3)_2$ $\mu g/g$	^{86}Sr $Sr(NO_3)_2$ $\mu g/g$	^{88}Sr $Sr(NO_3)_2$ $\mu g/g$
Ag	^{109}Ag	0.4ᵃ	0.03	0.1
Al	26	0.4ᵃ	0.1	0.5
As	^{80}Se	0.03ᵃ	—	—
Baᵇ	^{135}Ba	—	12.5	0.73
Bi	^{203}Tl	0.04ᵃ	—	—
Caᵇ	^{42}Ca	0.10ᶜ	0.78	0.30
Cd	^{111}Cd	0.01ᵃ	0.01	0.01
Ce	^{142}Ce	0.004ᵃ	0.02	0.2
Co	^{62}Ni	0.01ᵃ	—	—
Cr	^{53}Cr	0.05ᵃ	0.07	0.06
Cu	^{65}Cu	0.04ᵃ	0.30	0.2
Fe	^{54}Fe	0.3ᵃ	0.54	1.2
Ga	^{71}Ga	0.02	0.01	0.01
In	^{113}In	0.01	0.01	0.01
K	^{41}K	0.05ᵃ	0.2	0.4
La	^{142}Ce	0.02ᵃ	—	—
Mg	^{26}Mg	0.2ᵃ	0.06	0.1
Mn	^{54}Fe	0.04ᵃ	—	—
Mo	^{97}Mo	0.12ᵃ	0.03	0.02
Na	^{41}K	2ᵃ	0.7	0.7
Nd	^{145}Nd	0.1	0.01	0.03
Ni	^{62}Ni	0.01ᵃ	0.03	0.06
Pbᵇ	^{206}Pb	0.04ᵃ	0.13	0.06
Sb	^{117}Sn	0.1ᵃ		
Se	^{82}Se	0.01ᵃ	0.01	0.01
Sn	^{117}Sn	0.3ᵃ	0.1	0.1
Te	^{125}Te	0.1ᵃ	0.05	0.08
Tl	^{203}Tl	0.05ᵃ	0.07	0.1
Ti	^{47}Ti	0.05ᵃ	0.02	0.06
V	^{53}Cr	0.01ᵃ	0.1	8.8
Zn	^{67}Zn	0.03ᵃ		
Zr	^{91}Zr	0.0021	0.01	0.01

ᵃ Doped with 1000 $\mu g/g$ of each element before purification.

ᵇ Analyzed by thermal ionization mass spectrometry.

washed twice with 0.5 mL portions of nitric acid which were removed in the same manner and combined with the acid from the crystallization. This nitric acid was concentrated to a small drop, evaporated to dryness on high purity gold wires, and analyzed by spark-source mass spectrometry. The results of this analysis are also shown in table 1.

In addition to the spiked elements, a number of other elements were determined by comparison to spiked nuclides and assuming that the sensitivities of the natural element and spike nuclide are the same.

Three elements, Ba, Pb, and Ca were determined by thermal ionization mass spectrometry since they were not obtained from the spark source analysis. Barium and lead are co-crystallized with the $Sr(NO_3)_2$ and calcium could not be determined because of Sr interference ($M/Z = 44$ for $^{88}Sr^{++}$). About 0.2 g samples were spiked with ^{206}Pb, ^{42}Ca, and ^{135}Ba. Calcium was separated in the same manner as the separation for the spark source analysis. Lead was separately electro-deposited from a nitrate solution onto a platinum anode. Barium was separated by adding lead and co-precipitating it with lead chromate by the addition of ammonium chromate. The chromates were caught on a filter and dissolved with 1.5 mol/L HCl. Lead and chromate ions were removed by passing the solution through a strongly basic anion exchange column, and the barium was recovered by evaporation of the eluate. The concentration of each analyte was determined from isotope ratio measurements using thermal ionization mass spectrometry.

The results of these analyses are also shown in table 1. Barium, which was not removed by the purification, was determined to be 12.5 µg/g in the $^{86}Sr(NO_3)_2$ and 0.73 µg/g in the $^{88}Sr(NO_3)_2$. This would cause an error of about 0.002 percent in the ^{86}Sr assay and <0.001 percent for the ^{88}Sr assay. Since these errors are not significant, corrections were not applied. No other element was found at a level high enough to cause a possible significant error in the assay procedure.

2.4. Preparation and Assay of the Separated Isotopic Solutions

The 4.3 g of purified $^{86}Sr(NO_3)_2$ was dissolved in about 50 mL of 0.5 mol/L HNO_3, transferred to a specially constructed and tared 500 mL quartz flask and diluted to about 500 mL with 0.5 mol/L HNO_3. This flask was constructed from a 500 mL quartz flask by cutting the neck of the flask about 1 cm from the body and tooling the neck for a number zero polyethylene stopper and standard aluminum serum cap.

The 4.3 g of purified $^{88}Sr(NO_3)$ was also dissolved in about 50 mL of 0.5 mol/L HNO_3, transferred to a specially constructed 200 mL quartz flask and diluted to about 200 mL with 0.5 mol/L HNO_3. This flask was constructed in the same manner as described for the 500 mL flask. The bottles and contents were weighed to ±0.2 mg and the preliminary strontium concentration was calculated. The solution of $^{86}Sr(NO_3)_2$ was designated "Sr 86" and the solution of $^{88}Sr(NO_3)_2$ was designated "SR 88".

Four weighed portions each containing about 1.6 mmol of strontium (~16 g each for the ^{88}Sr solution and ~40 g each for the ^{86}Sr solution) were withdrawn from each separated isotope solution in the following manner: a 10-cm platinum needle was inserted through a No. 0 polyethylene stopper which was used to replace the cap in the bottle. A 10-mL polyethylene hypodermic syringe with the plunger covered with a thin sheet of Teflon was attached to the Kel-F hub of the needle and the desired amount of solution was withdrawn. The syringe was then disconnected from the hub and the tip was capped with a Kel-F cap. Any static charge that might be present on the plastic syringe was dissipated by wiping it with a damp lintless towel. The syringe and contents were weighed on a semimicrobalance to ±0.02 mg. The solution was then delivered from the syringe into a 100 mL Teflon-FEP beaker and the syringe was again capped, wiped, and weighed. The weight of the sample was determined from the weight of the syringe before and after delivery of the sample. Two assay samples were withdrawn from each solution before and after withdrawing the calibration samples to ensure that no change in concentration had occurred during this time interval (about 3 h).

Each portion was then assayed as follows: 1 mL of perchloric acid was added and the solution was evaporated at low heat to fumes of $HClO_4$. The solution was then cooled, taken up in a few mL of water, and again evaporated to fumes of $HClO_4$. This procedure was repeated and the excess perchloric acid was removed by evaporation. (This procedure converts $Sr(NO_3)_2$ to $Sr(ClO_4)_2$ and is necessary because nitrate causes significant errors in the determination of strontium as sulfate.)

The residue was taken up in 20 mL of water and heated. Fifteen mL of warm (1 + 99) H_2SO_4 was added dropwise to the hot solution while swirling the beaker to precipitate $SrSO_4$. The sulfuric acid was added at a rate that required about 15–20 min to complete the addition. The solution was heated at 80–90 °C for 2 h and evaporated to about 15 mL of solution. Fifteen mL of 95 percent ethyl alcohol was added and mixed with the solution. After tightly covering the beaker with plastic film, it was allowed to stand overnight to complete the precipitation.

The solution was then filtered through a tared platinum Monroe crucible and the precipitated strontium sulfate was caught on the platinum mat. Any $SrSO_4$ adhering to the walls of the beaker was freed by scraping with a Teflon "policeman" and transferred to the crucible with a stream of 95 percent ethyl alcohol. The filtrate, washings, and Teflon "policeman" were transferred back to the original beaker and reserved for the determination of dissolved and untransferred strontium. The crucible and contents were dried for 2 h at 105 °C,

ignited at 800 °C for 8 h, cooled in a desiccator, transferred to the case of a micro-balance and allowed to stand for at least 2 h. The crucible and contents were weighed on the micro-balance to ±0.002 mg. A buoyancy correction for platinum crucibles was made by averaging three empty tare crucibles. (The drying, cooling, and weighing were repeated to insure constant weight.) The air weight of the $SrSO_4$ was then determined and converted to vacuum weight using 3.92 for the density of $^{86}SrSO_4$ and 3.97 for the density of $^{88}SrSO_4$. These densities were calculated by assuming that they were proportional to the density of natural $SrSO_4$, 3.96 in the same relationship as their molecular weight. The vacuum weight of the strontium sulfate was converted to millimoles of strontium using a calculated atomic weight for strontium and the 1977 atomic weight values for sulfur and oxygen. The formula weights used were 182.0066 for the $^{86}SrSO_4$ and 183.9612 for the $^{88}SrSO_4$.

To determine the soluble and untransferred strontium, the filtrate and washings which had been reserved in the original beaker were spiked with about 1.5 mmol of ^{84}Sr. The ^{84}Sr was NBS SRM 988, Strontium 84 Spike Assay and Isotopic Solution Standard. The solution was heated and concentrated to about 10 mL to remove ethyl alcohol. Fifteen mL of HCl and 5 mL of (1 + 99) H_2SO_4 were added, and the solution was diluted to 100 mL with water. The solution was then heated for two hours to ensure equilibration of the natural and spike strontium. The solution was evaporated to fumes of perchloric acid and then the heat was increased to fumes of sulfuric acid. After cooling, the residue was taken up in 15 mL of water and passed through a cation exchange column, containing 5 mL of AG50Wx8, resin. The column was then washed with 50 mL of 0.5 mol/L HCl and the Sr was eluted with 25 mL of 6 mol/L HCl. This solution was evaporated to dryness. The residue was converted to the nitrate by the addition of a few drops of nitric acid followed by evaporation. The residue was taken up and the 84/86 or 84/88 ratio was

determined by thermal ionization mass spectrometry. The Sr found as mmol Sr was added to the strontium from the gravimetric determination to yield the total strontium in the sample.

This method of determining the strontium was first tested on solutions containing known amounts of strontium. Ten solutions were prepared from high purity strontium carbonate. The material used was SRM 987, Strontium Carbonate, which has an assay value of 99.98 ± 0.02 percent. The solutions were prepared in the approximate concentration range of 0.10 to 0.12 mmol/g. Four samples containing from 1.50 to 1.79 mmol were withdrawn from each solution and the strontium was determined as described above. Comparison of the calculated to measured concentration detected a small positive bias of about 0.01 percent, but this would have a negligible effect on ratios.

The results of the assay of the separated isotope solutions are shown in table 2. Pooling the results of the separated isotope solutions and the ten sets described above, yields an uncertainty of 0.119×10^{-5} mmol/g for the concentration of the "Sr 86" solution and 0.297×10^{-5} mmol/g for the concentration of the "Sr 88" solution.

2.5. Preparation of Calibration Samples

Six calibration samples were prepared by mixing weighed portions of "Sr 86" and the "Sr 88" solutions to produce 88/86 ratios, ranging from 8 to 0.7. Four of the calibration samples were within a few percent of the natural 88/86 ratio of 8.38 and two bracketed the natural 87/86 ratio of 0.71. The portions were withdrawn from the flasks and weighed in the manner previously described for assay of the solution. To eliminate any possibility of change in the concentration of the isotope solution with time, the portions for the calibration samples were withdrawn from the flasks between the samples taken for assay over a period of about 6 h.

TABLE 2. *Assay of Strontium Separated Isotope Solutions Separate I*

Solution	Sample No.	Weight $SrSO_4$ (vac) g	Sr from $SrSO_4$ mmol	Sr from Filtrate mmol	Total Sr mmol	Weight Sample g	Conc. Sample mmol/g
^{86}Sr	1	0.293588	1.613062	0.002681	1.615743	40.89026	0.0395141
	2	.296739	1.630375	.001504	1.631878	41.30356	.0395094
	3	.293032	1.610006	.003275	1.613281	40.82803	.0395141
	4	.298813	1.609352	.002365	1.611717	40.78996	.0395126
	Average						.0395175
^{88}Sr	1	0.320318	1.741227	0.001667	1.742894	17.64999	0.098748
	2	.302946	1.646795	.001854	1.648649	16.69340	.098761
	3	.301413	1.638460	.001616	1.640076	16.60703	.098758
	4	.310012	1.685206	.002920	1.688126	17.09511	.098749
	Average						.098754

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Table 3 shows the composition of these calibration samples. The isotope ratio of each calibration sample was calculated from the isotopic analysis of the separated isotopes and from the mmols of strontium from each separated isotope solution as determined from the assay and weight of solution taken.

Each calibration sample was thoroughly mixed and evaporated to dryness at low heat on a hot plate. The calibration samples were taken up in (1 + 49) nitric acid so that 1 mL of solution contained 500 μg of strontium.

3. Results and Discussion

Isotopic compositions of the purified ^{86}Sr and ^{88}Sr were each measured by Operator #1, using 7–10 sample analyses for each separated isotope. Before and after each set of separated isotope analyses, the ion source was removed from the instrument and meticulously cleaned. Prior to each set of separated isotope analyses, the source was carefully checked

to insure the absence of any cross contamination. The results of the measurement of the separated isotope solutions are shown in table 4.

The six synthetic isotope mixes were selected randomly and measured two or three times by each operator for its $^{88}Sr/^{86}Sr$ ratio. SRM 987 was analyzed after every two mixes, and the average of these SRM analyses provided the data used in the final computation of the absolute abundance ratios of the reference sample.

The results of the measurements of the separated isotope mixtures as well as the correction factors for each operator are shown in table 5.

In Table 6 are shown ratios for the reference material (SRM 987–Strontium Carbonate) for each operator.

The calculations of the atomic weight of the reference sample of strontium are shown in table 7. The value calculated is only applicable to the reference material (SRM 987) since samples in nature with large variations in the $^{87}Sr/^{86}Sr$ ratios

TABLE 3. *Isotopic Composition of Calibration Samples*

Solution No.	Isotope Solution	Weight Solution g	Sr from Solution mmol	^{86}Sr from Solution mmol	^{88}Sr from Solution mmol	Total ^{86}Sr Solution mmol	Total ^{88}Sr Solution mmol	Ratio 88/86 Solution
1	"Sr 86"	5.05855	0.199876	0.195191	0.003349			
.	"Sr 88"	16.28401	1.608108	.000741	1.605506	0.195932	1.608855	8.211280
2	"Sr 86"	4.94747	0.195487	.190905	0.003276			
	"Sr 88"	16.45020	1.594893	.000735	1.592313	.191640	1.595589	8.325967
3	"Sr 86"	4.98057	0.196795	.192182	0.003298			
	"Sr 88"	16.50848	1.630275	.000751	1.627637	.192934	1.630935	8.453349
4	"Sr 86"	5.20231	0.205557	.200738	0.003444			
	"Sr 88"	17.41636	1.719931	.000793	1.717149	.201531	1.720593	8.537609
5	"Sr 86"	17.91602	1.707908	.691315	0.011862			
	"Sr 88"	5.02571	0.496308	.000229	0.495505	.691543	0.507367	0.733673
6	"Sr 86"	18.24981	0.721097	.709195	0.012083			
	"Sr 88"	4.89190	0.483094	.000223	0.482312	.704417	.494395	.7018501

TABLE 4. *Isotopic Composition of Separated Strontium Isotopes Used in Calibration Samples*

Separated Isotope	Isotopic Composition Atom Percent	
"Sr-86"	88	1.673483 (365)[a]
	87	0.655174 (384)
	86	97.658689 (721)
	84	0.012651 (507)
"Sr-88"	88	99.838084 (260)
	87	0.115774 (234)
	86	0.046142 (110)
	84	0 (<4 ppm)

[a] Numbers in brackets are the errors (95% confidence limits) on the last digits of the numbers given.

are known. Subsequent to the Faraday cage measurements described here, high sensitivity pulse counting measurements in this laboratory have indicated the possibility of sporadic backgrounds at the $M/Z = 86$ position of $\sim 10^{-16}$ A. Although the background has tentatively been identified as a hydrocarbon residue resulting from previous exposure to resin beads in the specific pulse counting system (not either instrument used in the Sr measurements), an extra allowance of 0.01 percent has been added to the systematic error of the $^{88}Sr/^{86}Sr$ and $^{87}Sr/^{86}Sr$ ratios as a precaution.[3]

It should be noted that the value of the $^{86}Sr/^{88}Sr$ ratio of 0.119351 is very close to the less precise value of 0.1194

universally used. The continued use of this historical value seems justified except where the very highest accuracy is required.

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[3] Recently published research [23] has demonstrated the formation of molecular parent and decomposition ions from quaternary ammonium salts (e.g., $M/Z = 86 = C_5H_{12}N^+$) in a conventional thermal ionization source. These data support the observation that exposure of the pulse counting mass spectrometer to anion exchange resin beads (quaternary ammonium salts) was the probable cause for background peaks in the strontium mass region for that specific mass spectrometer. Since: (a) the mass spectrometers used for strontium were never exposed to these resin beads; (b) all other measurement evidence in the strontium data do not reflect a statistically significant background; (c) no higher intensity molecular ion peaks were observed that one would expect to accompany those of the strontium mass region, we believe the isotope ratio data for SRM 987 to be free of systematic bias well within the stated error limits.

TABLE 5. *Determination of Mass Spectrometer Bias*

Calibration Sample No.	Isotopic Ratio $^{88}Sr/^{86}Sr$			Correction Factor	
	Calculated	Operator I	Operator II	Operator I	Operator II
1	8.211280	8.200908	8.197613	1.001265	1.001667
2	8.325967	8.315727	8.315177	1.001231	1.001298
3	8.453349	8.442254	8.443429	1.001314	1.001175
4	8.537609	8.527686	8.527326	1.001164	1.001201
5	0.733673	0.732628	0.732525	1.001426	1.001567
6	.701850	.700835	.700891	1.001448	1.001368
	Mean Values of Correction Factors			1.001308	1.001379
	Average		1.001344		

TABLE 6. *Isotopic Ratios of SRM 987, SrCO₃*

Ratio	Operator 1	Operator 2	Average Ratio[a]	Correction Factor	Corrected Ratio
$^{88}Sr/^{86}Sr$	8.3678911	8.36689550	8.3673671	1.0013439	8.378612
$^{87}Sr/^{86}Sr$	0.7099313	0.7098806	0.7098619	1.0006719	0.7103389
$^{84}Sr/^{86}Sr$	0.0566361	0.0566166	0.0566253	0.9986579	0.05654927

[a] Because no statistically significant differences were found between the data of operators 1 and 2 they were combined into a single set for the calculation of average ratio, correction factor, and corrected ratio. The appropriate error limits are given in Table 7.

TABLE 7. *Atomic Weight, Atom Percent, and Isotopic Ratios of Strontium (corrected for systematic errors)*

	Value	Total Uncertainty	Due to Error in Calibration Factor	Due to Error in Ratio Determination	Due to Systematic Error in Determination	Due to Error in Nuclidic Masses of Isotopes
Atomic Weight	87.616814	0.000117	0.0000477	0.0000266	0.0000397	0.0000029
Atom Percent						
Sr-84	0.55738	0.00155	0.000211	0.000412	0.00093	
Sr-86	9.85659	.00337	.001718	.000724	.00093	
Sr-87	7.00152	.00263	.000506	.000862	.00126	
Sr-88	82.58451	.00657	.002435	.001458	.00268	
Isotopic Ratios						
84/86	0.056549	0.000143	0.0000115	0.0000420	0.00009	
87/86	.710339	.000261	.0000725	.0000760	.00007	
88/86	8.37861	.003248	.0017070	.0007409	.00080	

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