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Superheavy Isotope Enrichment Using a Carbon Isotope Enrichment Plant

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Abstract

A ^{13}C isotope distillation separation plant was used to search for naturally-occurring superheavy isotopes. Superheavy (X^-) isotopes of carbon in CO would be only slightly less volatile than the normal $^{12}C^{16}O$. Over 100,000 mol CO were passed through the distillation columns without product withdrawal during the experiment. Following cessation of flows, 201 gas samples were collected from the bottom of the high enrichment column. An argon impurity in the CO provided a "wedge" to enrich X^- isotopes at the CO/Ar interface in the column. Carbon isotopic compositions were used to calculate which samples might contain the superheavy isotopes. Enrichments of X^- isotope concentration of ~10^5 were obtained in several 0.1 mol samples, which were analyzed for the existence of X^- isotopes at another laboratory. A limited amount of extremely pure ^{13}CO was produced as a side benefit.

INTRODUCTION

Particle physicists have theorized the existence in nature of anomalously heavy particles (1000 amu and greater) which are stable and date from the origin of the universe (*1*). These remnants of the big bang would be quite scarce but potentially detectable if they are charged. If a massive negatively charged particle, X^-, attaches to a normal nucleus of element Z, a superheavy isotope of element Z − 1 is formed. Thus an X^- particle entering the earth's atmosphere could strike the nucleus of a nitrogen atom and produce a superheavy carbon isotope. These X^- isotopes have not been found in experimental searches, but researchers have set upper limits on the concentrations of such particles (*2–6*). By using samples enriched in X^- particles relative to natural samples, it should be possible to either find the X^- or reduce upper limits on their abundance.

Although an X^- isotope of an element is grossly more massive than normal isotopes, its chemical properties are not as different as might be expected. Popowicz and Bigeleisen have calculated that a carbon isotope of mass 1000 in carbon monoxide has a vapor pressure 10% lower than that of $^{12}O^{16}O$ (*7*). Even higher mass carbon isotopes would have essentially the same volatility as ^{1000}C. By comparison, $^{13}C^{16}O$ has a vapor pressure 1% lower than $^{12}C^{16}O$ (*8*). This suggests that an X^- may be treated as a normal isotope in an isotope separation process.

Los Alamos has very long ^{13}CO isotope distillation columns (*9*) which had been put on standby status due to large inventories. These columns were used to attempt to enrich X^- isotopes along with the normal isotopes by operating for an extended period with no product withdrawal. Gas was withdrawn at the end of the experiment, and samples were analyzed by an electrostatic charged particle spectrometer at the University of Rochester. Thus this was a rare opportunity to use a production facility for a research experiment.

EXPERIMENTAL

The ^{13}C holdup in the columns had been previously withdrawn to a low level, thus it was expected any X^- separated by earlier operations had also been removed. All gas-handling lines were retested for leaks with a helium leak detector.

The Los Alamos ^{13}C isotope separation plant consists of two packed columns in series, with 3000 and 2750 theoretical plates (Fig. 1). The packed heights of these two columns are 210 and 55 m, respectively. An initial cryogenic purifier removes the high-boiling impurities CO_2 and $Fe(CO)_5$ which would condense as solids in the columns at 80 K. A cryogenic distillation column purifier removes nitrogen from the feed gas. In previous operations, another distillation column was used to remove less volatile impurities (notably argon) in the CO feed. This second column purifier was not used for this experiment because it would likely also remove any X^- in the feed stream.

Under normal operating conditions, the first isotope column produces about 80% ^{13}C and 5% ^{18}O in the bottom drawoff gas stream. This gas then flows through an isotopic equilibrator, which uses alumina catalyst pellets to achieve isotopic exchange equilibrium (*10*). Following equilibration, the gas is fed to the high enrichment column. At this point most of the ^{18}O is in the form $^{13}C^{18}O$. Because ^{16}O is still the most abundant oxygen isotope at this point, most superheavy carbon isotopes present would remain attached to an ^{16}O.

Total gas fed to the plant was measured both by integrating the flow to the column and by measuring the drop of CO pressure in the feed tube trailer. Some CO gas was vented along with N_2 from the top of the purifying distillation column during purification. Because X^- isotopes have notably lower volatility relative to $^{12}C^{16}O$, little X^- isotope was lost in this stream.

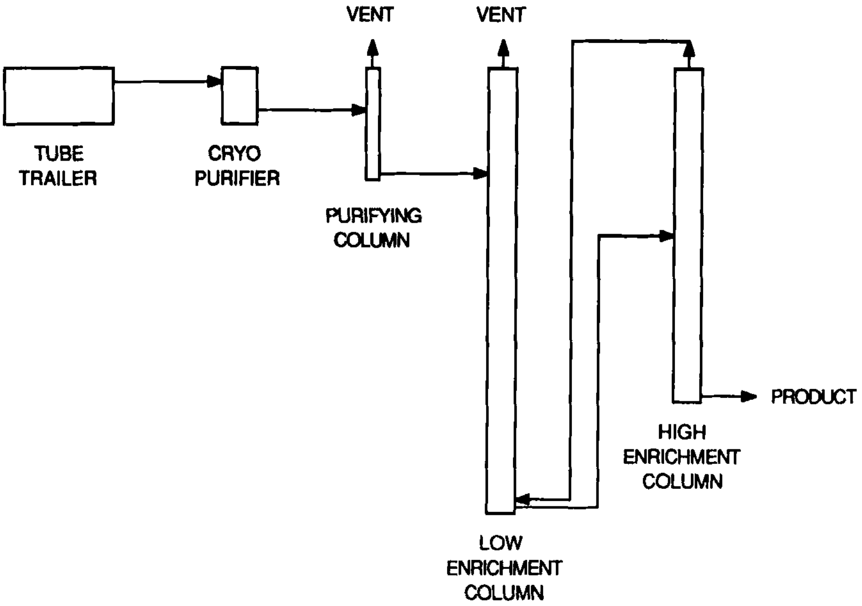

FIG. 1. CO isotope plant schematic.

The two measurements of CO usage are compatible with each other and the vent rate.

Most gas streams were analyzed periodically for isotopic content by using a CEC 21-621 cycloidal mass spectrometer. Besides CO isotopic species, argon was also observed in the bottom stream from the first enrichment column. As no gas was withdrawn from the bottom of the high enrichment column, this stream was not analyzed until the end of the experiment.

Following the special operation of the columns, samples of gas were withdrawn from the bottom of the high enrichment column into 37 identical stainless steel 958-cm^3 containers. Samples were immediately analyzed for gas and isotopic compositions on the CEC mass spectrometer. As the samples were analyzed, older samples were pumped away until samples likely to contain the X^- particles were collected.

RESULTS

Over the course of 5 months, 102,000 mol CO was used from the tube trailer, and a total of 81,300 mol CO was fed to the columns during the experimental run. The top waste stream of CO from the first isotope column typically contained 0.5% $^{13}C^{16}O$, about half the natural abundance. From this analysis and the calculated relative volatility of the X^- version of CO, over 99% of any X^- molecules present were retained in the isotope columns.

A total of 201 samples were collected and analyzed. The pressure of Samples 23–196 varied between 1780–1900 torr at 20°C, thus the majority of the samples contained 0.0933–0.0996 mol gas. For CO distillation in the high enrichment column, each theoretical plate corresponds to a packed height of 2 cm and a liquid holdup of 1.19 cm^3 (*9*). From the molar density of CO at the operating temperature of the lower part of this column (~90 K), this is 0.032 mol CO per plate. Thus for CO we expect the isotopic separation between consecutive samples to be equivalent to that of 3.0 theoretical plates.

The first sample collected from the high enrichment column was mostly CO, representing the "dead" volume of the drawoff line, but the fraction of CO fell to 0.3% by the fourth sample and was not observed at all by the sixth. Argon was the major constituent of Sample 2 and all succeeding samples through 182. Up to 3.7% methane was found in Samples 3–11, but none was observed in subsequent samples. The column drawoff line was partially plugged during the first seven samples, possibly due to higher hydrocarbons. No plugging was observed as later samples were withdrawn.

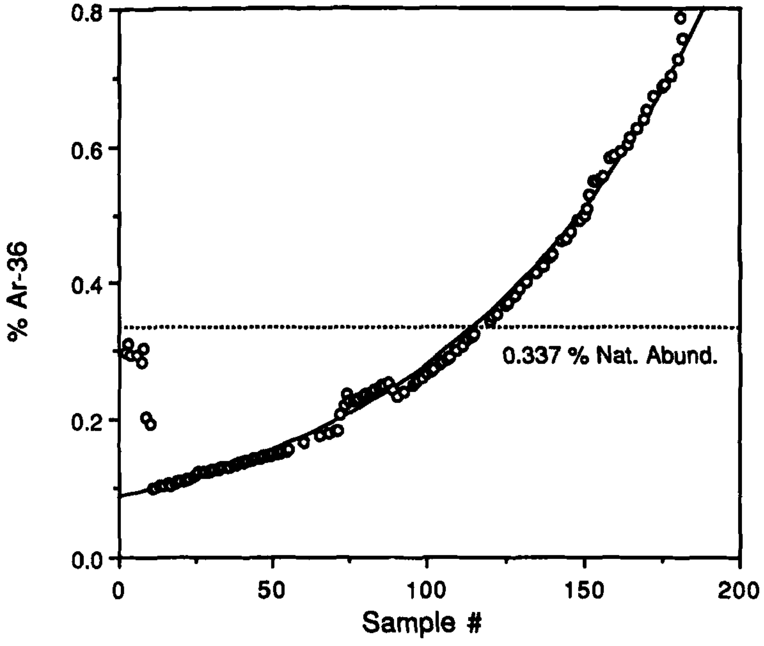

FIG. 2. ^{36}Ar isotopic composition profile.

Isotopic separation of argon isotopes was quite evident in the first 180 samples. Figures 2 and 3 show the isotopic compositions of ^{36}Ar and ^{38}Ar increasing as the drawoff continued. Except for initial samples containing "dead" gas in the lines, the curves closely follow the expected exponential shape. The ^{36}Ar/^{40}Ar relative volatility is 1.0050 at 96.5 K (P = 1830 torr) (*11*), and one can safely estimate the ^{38}Ar/^{40}Ar volatility to be 1.0025, the square root of 1.0050. From these α's, the isotopic separations were 2.36 and 2.04 plates/sample ^{36}Ar and ^{38}Ar, respectively. The compositions of the minor argon isotopes were also of value in pointing to the onset of CO appearance. The average of the sample compositions should equal the natural abundance of the isotopes; thus the areas between the curve and the natural abundance line, above and below, should be equal.

In previous operation of the ^{13}C plant, the presence of argon in the ^{13}C product has been regarded as bothersome, at best. However, the presence of argon was vital to the success of this experiment. Since $^{13}C^{18}O$ is about 1.07 times as volatile as the X$^-$ CO and about 1.6 times as volatile as ^{40}Ar, the X$^-$ isotopes should be concentrated near the point in the column where

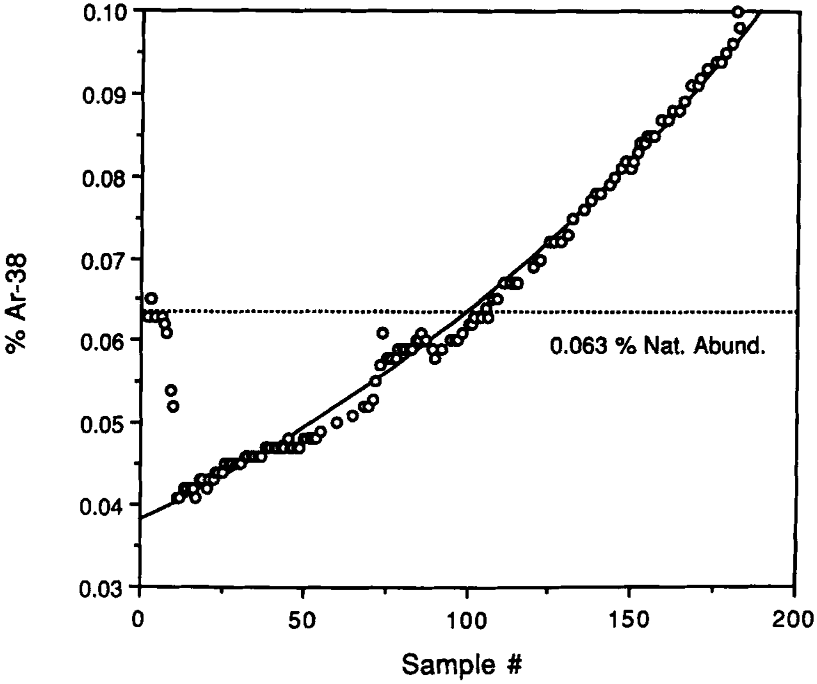

FIG. 3. ^{38}Ar isotopic composition profile.

TABLE 1

Sample Compositions

Sample	%29	%30	%31	%36	%38	%40
180			0.001	0.725	0.096	99.178
181	0.119	0.007	0.210	0.784	0.100	98.780
182	5.273	0.173	9.255	0.645	0.084	84.570
183	24.657	0.784	42.330	0.245	0.033	31.951
184	32.517	1.045	56.178	0.071		10.189
185	35.359	1.130	60.573	0.022		2.916
186	36.358	1.157	61.555			0.930
187	36.967	1.170	61.587			0.276
188	37.275	1.175	61.445			0.106
189	37.537	1.179	61.190			0.094
190	37.745	1.183	61.034			0.038
191	38.087	1.185	60.728			
192	38.342	1.189	60.469			
193	38.503	1.189	60.308			
194	38.752	1.192	60.057			
195	39.025	1.194	59.780			
196	39.244	1.197	59.559			

CO just begins to appear. The first evidence of CO was found in Sample 180, and the gas in Sample 187 was >99.5% CO. No $^{12}C^{16}O$ was observed in these samples. Table 1 gives data for Samples 180–196.

DATA ANALYSIS

As the X^- isotopes cannot be detected by conventional mass spectrometers, the X^- isotope concentration profile must be calculated from data on other isotopes.

The high enrichment column operated at total reflux in the area of the column bottom throughout the experiment. During sample collection, the total amount of gas withdrawn was small compared to the total holdup. Thus the samples can be considered to represent a composition profile of the lower part of the column at the end of the experiment.

For a distillation column operating at total reflux with known compositions at one point, $x_1^\circ, x_2^\circ, \ldots, x_n^\circ$, compositions at other points in the column are given by

$$x_i = \frac{x_i^\circ e^{-N \ln \alpha_i}}{\sum_{j=1}^{n} x_j^\circ e^{-N \ln \alpha_j}} \tag{1}$$

Here N is the number of theoretical plates below the reference point, and the α's are volatilities relative to the lightest component.

Column pressure was relatively constant at 1835 torr while Samples 180–196 were withdrawn. However, because the column composition changed from pure argon to pure CO during this transition, the temperature of the liquid vaporized for these samples dropped some 6°. The temperatures of pure, normal isotopic Ar and CO at 1835 torr vapor pressure are calculated to be 96.7 and 90.2 K, respectively, from vapor pressure data (*12*) and using the integrated form of the Clausius-Clapeyron equation

$$\ln \frac{P_2}{P_1} = -\frac{\lambda}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{2}$$

The relative volatilities of the isotopic components vary as a function of temperature. Table 2 lists computed relative volatilities at different temperatures based upon $^{12}C^{16}O$. Results from Ref. 7 were used to compute the CO isotopic α's, and Eq. (2) and Ref. *12* were used for ^{40}Ar α's.

As a first attempt to find the location of maximum X^- isotopes, take the point in the column where argon composition is 50% as the reference point. From Eq. (2) the temperature at this point is about 93.6 K. Let us consider the argon to be totally ^{40}Ar and the CO to be solely a 1:1.7 mixture of $^{13}C^{16}O$ and $^{13}C^{18}O$. The ln α of Ar relative to the average CO is then -0.5456, and the ln α of the X^- isotopes is -0.06309. We can now develop a relation for the variation in composition of X^- isotopes in the vicinity of this point in the column. There is an infinitesimally small amount of X^- isotopes, thus they do not contribute to the denominator of Eq. (1).

$$\frac{x_X}{x_X^{\circ}} = \frac{e^{0.06309N}}{0.5 + 0.5e^{0.5456N}} \tag{3}$$

TABLE 2

Volatilities Relative to $^{12}C^{16}O$

Compound	ln α (90.2 K)	ln α (93.5 K)	ln α (96.7 K)
$^{12}C^{16}O$	0.0	0.0	0.0
$^{13}C^{16}O$	−0.00555	−0.00517	−0.00483
$^{13}C^{17}O$	−0.00758	−0.00706	−0.00660
$^{13}C^{18}O$	−0.00941	−0.00876	−0.00819
$^{1000}C^{16}O$	−0.0796	−0.0741	−0.0692
^{40}Ar	−0.5649	−0.5530	−0.5454

The point of maximum concentration of X^- isotopes may be found by differentiating Eq. (3) and setting it equal to zero. With some rearrangement:

$$N = \frac{1}{0.5456} \ln \frac{0.06309}{0.5456 - 0.06309} \tag{4}$$

and the maximum concentration occurs 3.7 plates down the column from the reference point. This is the equivalent of slightly more than one gas sample. From Table 1, Sample 184 probably contains the maximum X^- concentration.

A more total picture of the distribution of X^- isotopes is obtained by treating the column as having five components ($^{13}C^{16}O$, $^{13}C^{17}O$, $^{13}C^{18}O$, $^{1000}C^{16}O$, and ^{40}Ar) and applying Eq. (1) over Samples 180–196. Some complications arise in relating composition of sample bulbs to length along the column because of the difference in column temperature represented by the samples and the different molar volumes of liquid CO and Ar. In Samples 185–196, the material is nearly all CO, and using 3.0 plates/sample and relative volatilities at 96.7 K describes the macroscopic compositions extremely well. The value of 2.36 plates/sample obtained for the $^{36}Ar/^{40}Ar$ separation is consistent with the 2.0 cm plate height and 3.0 plates/sample when the differences in molar liquid volume are taken into account. Thus, one should vary slightly the number of plates/sample and the relative volatilities for Samples 180–184.

Figure 4 gives the relative variation of concentration of X^- isotopes in Samples 180–196. Calculations were made assuming a small mole fraction (10^{-6} in Sample 185) to avoid computational problems with a macroscopic composition; the actual mole fraction is far smaller. As was previously indicated, Sample 184 has the maximum concentration of X^- isotopes. The total amount of X^- isotopes is represented by the area under the curve. If one assumes that nearly all X^- in the column was collected in these samples, about half of all X^- in the column is in Samples 183–186. A total of 10^5 mol CO was fed to the column, and these samples contain 0.4 mol CO with half the total X^- isotopes, thus the X^- isotopic composition in Samples 183–186 was enriched by 10^5 over natural abundance.

DISCUSSION

Samples 184 and 185 were sent to the Nuclear Structure Research Laboratory of the University of Rochester for analysis using an electrostatic charged particle spectrometer. No X^- particles were detected; however, new upper limits for the existence of the X^- particle were established (*13*, *14*). The upper limit of existence was lowered to 10^{-20} at mass 400 compared to Turkevich's result of 10^{-15} (*2*).

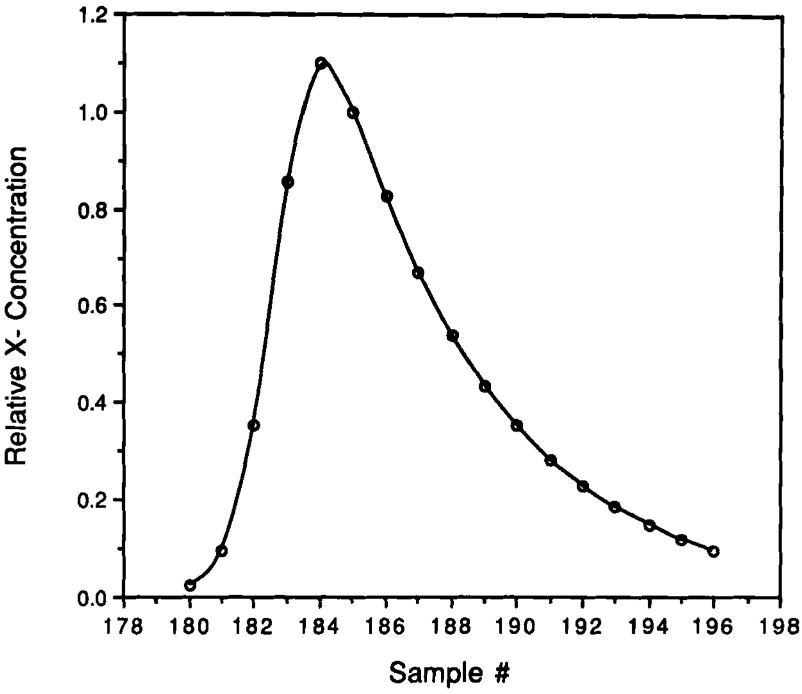

FIG. 4. Calculated X^- isotopic composition profile.

Samples collected from this experiment contain the most highly enriched ^{13}C material ever produced by this plant. The CEC mass spectrometer has a threshold of detectability of about 0.01%, and no $^{12}C^{16}O$ was observed in Samples 180–201. The least volatile isotopic species containing ^{12}C is $^{12}C^{18}O$, which is indistinguishable from $^{13}C^{17}O$, also at mass 30. The data may be used to imply which isotopic species are present, using Eq (1) and the calculated values of ln α of 0.001829 for $^{13}C^{17}O/^{13}C^{18}O$ and 0.005426 for $^{12}C^{18}O/^{13}C^{18}O$ at 90.2 K.

Figure 5 compares data for the ratio of masses 30/31 with the assumptions that mass 30 is either pure $^{12}C^{18}O$ or $^{13}C^{17}O$. Curves were fitted to the compositions for Sample 190. The data follow the $^{13}C^{17}O$ curve quite closely for Samples 188–196. Some divergence occurs for lower numbered samples, but this may be due to effects such as the presence of an Ar/CO mixture and the rapid change in column temperature. The slope of data for Samples 184–186 matches the $^{13}C^{17}O$ slope.

If one assumes that at least 90% of the mass 30 CO is $^{13}C^{17}O$, the lower limit on concentration of ^{13}C in these samples is 99.9%. A more accurate analysis might be obtained by using high resolution mass spectrometry.

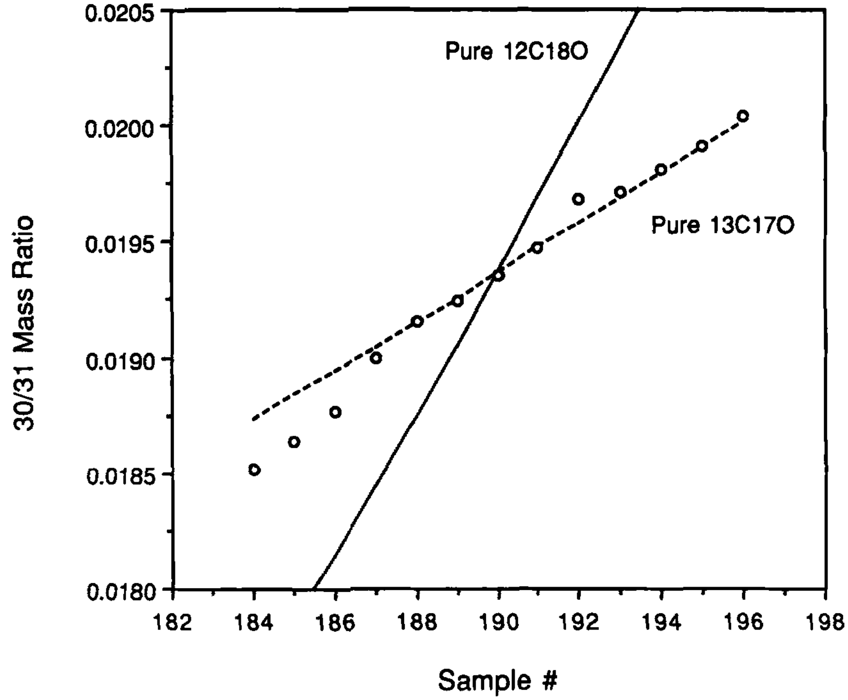

FIG. 5. Mass 30 CO isotopic composition profile.

CONCLUSIONS

It is possible to operate an isotope distillation plant in a nonproduction mode to obtain unusual enrichments of heavy isotopes without operating difficulty. The concentration profile at the column bottom is found by withdrawing consecutive samples of the holdup. Concentration profiles can be described by the equation for a column at total reflux. As a result of the enrichment obtained, physicists have lowered the upper limit on possible levels of X^- particles (as carbon isotopes) by a factor of 10^5. As a side benefit, the experiment produced several moles of exceptionally high enrichment ^{13}CO which may be of interest to other researchers.

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