A Study of the Trace ^{39}Ar Content in Argon from Deep Underground Sources

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Abstract

The discovery of argon from deep underground sources with significantly less ^{39}Ar than atmospheric argon was an important step in the development of direct dark matter detection experiments using argon as the active target. We report on the design and operation of a low-background single-phase liquid argon detector that was built to study the ^{39}Ar content of this underground argon. Underground argon from the Kinder Morgan CO_2 plant in Cortez, Colorado was determined to have less than 0.65% of the ^{39}Ar activity in atmospheric argon, or 6.6 mBq/kg specific ^{39}Ar activity.

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1. Introduction

Argon has been considered as an excellent medium in the direct detection of Weakly Interacting Massive Particles (WIMPs). Argon-based scintillation detectors can make use of pulse shape discrimination (PSD) to separate WIMP-induced nuclear recoil signals from electron recoil backgrounds with extremely high efficiency ($\sim 10^8$, with potential improvement to 10^{10}) [1, 2, 3]. Argon-based detectors can also be operated as ionization detectors, or as two-phase scintillation-ionization Time Projection Chambers (TPCs) [4] that have even more background suppression capability.

Argon-based WIMP dark matter searches, however, must confront the presence of intrinsic ^{39}Ar , a beta emitter with an endpoint energy of 565 keV and half-life of 269 years. ^{39}Ar is present at an activity of ~ 1 Bq/kg in atmospheric argon [5]. Even with PSD, the ^{39}Ar activity in atmospheric argon limits the ultimate size of argon-based experiments and restricts their ability to probe very low energy events.

The ^{39}Ar activity in the atmosphere is mainly produced and maintained by cosmic ray induced nuclear reactions such as $^{40}\text{Ar}(n,2n)^{39}\text{Ar}$. Because of the long lifetime of ^{39}Ar , the only practical way to reduce the amount of ^{39}Ar in atmospheric argon is isotope separation. This is possible, but costly and time consuming for ton-scale argon detectors.

Most of the ^{40}Ar in the atmosphere was produced by electron capture decays of long-lived ^{40}K within the Earth and much of the ^{40}Ar produced remains underground. It might be expected that argon from underground sources would have less ^{39}Ar radioactivity since cosmic rays can be efficiently attenuated by rocks. Unfortunately, as shown in studies by Loosli, Lehmann and Balderer [6] and Lehmann [7], ^{39}Ar can be produced underground by the (n,p) reaction of radiogenic neutrons on stable potassium, $^{39}\text{K}(n,p)^{39}\text{Ar}$. The average ^{39}Ar concentration in crustal argon is not expected to be significantly lower than that in atmospheric argon. However, because the uranium and thorium content of rocks, which determines the local radiogenic neutron flux, varies in the crust, the ^{39}Ar concentration in underground argon vary from place to place, with measured ^{39}Ar levels ranging from 20 times lower to 16 times higher than the atmospheric value [7, 8].

34 A search was undertaken by the Princeton group for a large supply of
35 underground argon low in ^{39}Ar . An early promising measurement was made
36 on argon that was extracted from the crude helium in the National Helium
37 Reserve [9]. The ^{39}Ar content in this argon was measured to be less than 5%
38 of the level in atmospheric argon, using a low background gas counter in the
39 laboratory of H. H. Loosli in Bern, Switzerland. However, large scale argon
40 extraction from the National Helium Reserve was found to be impractical..

41 Compared to the Earth's crust, which has uranium and thorium at ppm
42 levels, the Earth's mantle is thought to contain these elements at the ppb
43 level [10]. Thus, the ^{39}Ar content in mantle argon could be a few orders
44 of magnitude lower than that in crustal argon. Measurements of isotope
45 abundances in the rare gases (helium, neon, argon, krypton, and xenon)
46 derived from CO_2 gas wells in the U.S. Southwest indicate that these gases
47 originate in the Earth's upper mantle [11, 12, 13], and thus these wells should
48 be a good source of argon low in ^{39}Ar . The crude gas from the National
49 Helium Reserve, on the contrary, was extracted from natural gas and is
50 believed to have a crust origin.

51 The argon gas extraction system used at the National Helium Reserve was
52 upgraded to increase its capacity, and deployed at the Reliant Dry Ice facility
53 on the Bravo Dome CO_2 gas field in Bueyeros, New Mexico. First samples
54 showed no sign of ^{39}Ar , but later measurements yielded evidence for ^{39}Ar
55 contamination, possibly due to a decrease in well pressure as the CO_2 was
56 consumed. The gas collection system was further upgraded and moved to the
57 Kinder Morgan CO_2 well in Cortez, Colorado. We are currently extracting
58 argon at this site at a rate of a few hundred grams per day [14]. At the
59 time of this writing, approximately 160 kg of underground argon has been
60 collected. The results presented in this work are based on kg-sized samples
61 of argon collected at Cortez in 2009 and 2011, which will be referred to as
62 the first sample and the second sample respectively in the discussions.

63 In this paper we describe a custom low-background liquid argon detec-
64 tor that was designed to improve the sensitivity and the robustness of the
65 ^{39}Ar measurement as compared to that in reference [9]. The detector is
66 described in Section 3. Using this approach, we obtained in 2011 a new,
67 more stringent upper limit of 0.65% on the ^{39}Ar abundance in the first argon
68 sample extracted from the Cortez site, relative to atmospheric argon (see
69 Section 4). This result demonstrates the highest sensitivity to ^{39}Ar in argon
70 of all known techniques [9, 15, 16, 17]. A follow-up measurement made in
71 2012 using the second underground argon sample obtained similar results

(see Section 5), indicating that the ^{39}Ar content in these wells has remained low. These limits for ^{39}Ar demonstrate that experiments using underground argon active volumes will significantly outperform those with atmospheric argon, especially in their sensitivity to low mass WIMPs. Moreover, even at the current upper limit of ^{39}Ar , dark matter searches using multi-ton scale argon detectors are practical with underground argon. The DarkSide-50 detector has been launched with the intention of using underground argon along with other innovative technologies for a sensitive dark matter search; it will also demonstrate near background-free operation in multi-ton argon detectors [18]. Detailed discussion on this work and its implications can be found in the Ph.D thesis [19].

2. Purification of Underground Argon

As described in Ref. [14], the raw carbon dioxide gas at the Cortez site is processed by a vacuum-pressure-swing adsorption (VPSA) unit that produces a crude mixture of approximately 40% nitrogen, 55% helium, and 5% argon by volume. A cryogenic distillation column was later constructed at FNAL to further purify the crude argon gas, which produced argon of $>99.9\%$ purity [20]. This system was used to provide the second underground argon sample for the 2012 measurement reported in this paper.

The first underground argon sample was collected before the distillation column existed, and it was purified at Princeton University using a zeolite column. The column contained 18 kg of Zeochem's Zeox Z12-07 zeolite in a 30 L aluminum gas cylinder, which absorbed the nitrogen content in the gas mixture and produced an effluent stream of concentrated argon and helium. This remaining gas was then passed through a 6L charcoal trap consisting of 2 kg of activated OVC 4x8 charcoal in a stainless-steel bottle immersed in liquid nitrogen. This cryogenic charcoal trap captured the argon while allowing the helium to escape. The product argon gas has a nitrogen concentration less than 1% by volume, and it has been demonstrated that further iterations of this process can bring the nitrogen level below 0.1% [19].

Both of the underground argon samples were further treated using hot calcium to remove the remaining impurities. A calcium trap, illustrated in Fig. 1, held trays that were filled with granules of $>98.0\%$ purity calcium within a Conflat-sealed stainless-steel cylinder. The calcium was heated above its melting point (842°C) for a short time, then the temperature was reduced slightly for the gettering action. The argon-rich gas was fed over the

Figure 1: The calcium trap used for argon purification.

hot calcium at ~ 1 L/min, allowing the calcium to react with the impurities in the stream. The stable solids produced by these reactions, including calcium nitride, remained in the trays, while argon, as a noble gas, passed through the trap and was collected in a cryogenic charcoal trap. The calcium trap could be refreshed by heating it above the melting point to expose a fresh layer of calcium; this cycle could be repeated until the calcium was largely consumed. Then the trap was opened, cleaned, and reloaded with fresh calcium. The calcium trap was also used in the inline purification as the argon gas was being filled into the detector for ^{39}Ar measurements.

The first underground argon sample had been stored in a Princeton laboratory with little overburden before the measurement in 2011. The surface storage of about three years is $\sim 1\%$ of the ^{39}Ar half life. Considering the equilibrium between ^{39}Ar decay and ^{39}Ar production in the atmosphere, the generation of ^{39}Ar in the sample during the storage period is a potential concern. However, the cosmogenic neutron flux at the Earth's surface is a few orders of magnitude lower than the average value in the atmosphere [21], suggesting that ^{39}Ar production at surface should be suppressed by a similar factor. A calculation using the COSMO code [22] confirmed that the equilibrium ^{39}Ar activity in argon stored on surface is only 1.7 mBq/kg, so after three years of surface exposure the activity will be $\ll 1.7$ mBq/kg, which would not be a concern to the experiment.

129 3. Apparatus

Figure 2: A schematic diagram of the low background detector. The active volume of liquid argon is surrounded by a PTFE cell coated with WLS, and viewed by a low background PMT. Copper and lead shielding reduce external backgrounds. An external liquid argon bath provides cooling for the inner detector.

130 The low background detector, as configured for the measurement of the
 131 first underground argon sample reported here, is illustrated in Fig. 2. It
 132 contained 0.56 kg of liquid argon as the active volume in a 2.5-inch inner
 133 diameter, 5.25-inch high “cup” made of highly crystalline PTFE. The inner
 134 surfaces of the PTFE container and the fused silica top window were coated
 135 with $\sim 300 \mu\text{g}/\text{cm}^2$ of p-Terphenyl [23, 24] via vacuum evaporation to shift
 136 the 128 nm ultraviolet argon scintillation light into the visible range. The
 137 photons were detected by a low background, high quantum efficiency ($>30\%$),

138 3-inch, Hamamatsu R11065 cryogenic photomultiplier tube (PMT) above the
 139 cup. The cup and PMT were enclosed within a 3.5-inch diameter copper and
 140 stainless steel sleeve, which was sealed at the top by a Conflat flange. The
 141 side and bottom of the sleeve were surrounded by 2 inches of oxygen-free
 142 high conductivity (OFHC) copper shielding; a loose-fitting 2.5-inch thick
 143 copper plug was inserted into the sleeve above the PMT to complete the
 144 inner shielding.

145 The inner detector and the copper shielding around it were cooled by a
 146 bath of commercial liquid argon in an open cryostat. The liquid level in the
 147 cooling bath was maintained by a model LC10 Teragon Research liquid level
 148 controller attached to a low pressure liquid argon supply dewar. The open
 149 cryostat sat within, and was supported by, a lead castle that was 8 inches
 150 thick on the sides, 12 inches thick on the bottom, and 4 inches thick on the
 151 top. A muon veto system, composed of 2 inches thick plastic scintillator
 152 panels, covered the sides and top of the lead.

Figure 3: The gas handling system for the low background argon detector. The underground argon could be purified as the detector was filled, and fully recovered without loss with the liquid nitrogen cooled charcoal trap.

153 The components of the low background detector gas handling system,
 154 shown in Fig. 3, were connected with copper tubing and Swagelok fittings.

155 The gas plumbing and the detector could be evacuated using a turbo-molecular
 156 pump (Pfeiffer Vacuum HiCube), with typical vacuum levels of 10^{-6} mbar
 157 achieved. When the detector was being filled, the argon gas was purified
 158 using both the calcium trap described earlier and a Mono-Torr zirconium
 159 getter to remove impurities such as water, oxygen, and nitrogen before being
 160 condensed in the pre-cooled detector volume. To empty the detector, cooling
 161 was stopped and as the underground argon evaporated it was recovered by
 162 condensing it in a charcoal-filled aluminum gas cylinder partially immersed
 163 in a bath of liquid nitrogen. The use of LN₂-cooled activated charcoal al-
 164 lowed for transfer and recovery of the argon without the use of mechanical
 165 compressors that could introduce impurities.

166 Data acquisition was carried out using 12 bit, 250 MHz digitizers (CAEN
 167 V1720). The output of the inner detector PMT was digitized directly. The
 168 signals from the ten PMTs of the muon veto system were processed by LeCroy
 169 623B amplitude discriminators, the output of which was logically summed
 170 and fed into a second digitizer channel. Readout of both digitizer channels
 171 was triggered by an amplitude discriminator on the inner PMT channel. For
 172 each event, 15 μ s of data were recorded, beginning 5 μ s before the trigger.

173 4. Measurement of the First Underground Argon Sample

174 The detector was commissioned in a ground-level laboratory at Prince-
 175 ton University, and later relocated underground at a depth of ~ 1450 meter
 176 water equivalent (m.w.e.) in the Kimballton Underground Research Facil-
 177 ity (KURF) in Virginia. In each measurement campaign, the detector was
 178 operated with samples of atmospheric and underground argon. The data
 179 presented here were obtained in 2011.

180 4.1. Data Processing

181 The energy response of the detector was monitored using a 10 μ Ci ¹³⁷Cs
 182 source that could be introduced between the lead shielding and the cryostat
 183 containing the liquid argon bath. As shown in Fig. 4, the relative light yield
 184 decreased slowly with time ($\sim 0.6\%$ per day) as impurities released from inner
 185 detector components accumulated. Given the relatively short duration of
 186 each measurement (typically one week), it was efficient to monitor and correct
 187 the drift in the light yield with calibration data, instead of implementing an
 188 in-run purification system.

Figure 4: Relative light yield degradation in the atmospheric argon data measured at KURF; errors are smaller than 1%.

189 After the energy scale of both atmospheric argon data and underground
 190 argon data was corrected to produce matching ^{137}Cs spectra, the under-
 191 ground argon spectrum was subtracted from the atmospheric argon spectrum
 192 and the resulting ^{39}Ar spectrum was fitted to the theoretical one with energy
 193 resolution applied. This fit provided the absolute energy scale of the detec-
 194 tor, which correctly included the spatial variation of light collection efficiency
 195 in the sensitive volume ⁶. Throughout this paper, energy is given in keV_{ee}
 196 (electron equivalent energy), assuming a linear scintillation response scaled
 197 from the ^{39}Ar calibration data. While quenching occurs for nuclear recoil
 198 events and low energy electron recoil events [25], the linearity assumption
 199 holds well for the particles and energy range of interest for this analysis.

200 The light yield of the detector was evaluated by using the single pho-
 201 toelectron (p.e.) pulses as a reference. In the runs at Princeton, typical
 202 light yields of 6 - 7 p.e./ keV_{ee} were observed at a slow component lifetime of
 203 1.45-1.55 μs (corrections from relaxation of slow argon scintillation were not
 204 applied). The uncorrected light yield in the KURF measurement was lower,
 205 at ~ 5 p.e./ keV_{ee} with a lifetime $\sim 1.3 \mu\text{s}$.

206 The time profile of liquid argon scintillation pulses depends strongly on

⁶The ^{137}Cs source was found to produce slightly different spectra at different calibration positions. This effect was attributed to spatial non-uniformities in light collection efficiency within the liquid argon volume.

Figure 5: F_{prompt} vs. energy in the atmospheric argon data measured at KURF. Electron recoil events form the bottom band with $F_{\text{prompt}} \sim 0.3$, and nuclear recoil events form the top band with $F_{\text{prompt}} \sim 0.75$.

the density of ionization produced by the exciting particle, and thus the pulse shape of the scintillation signal can be used to distinguish electron recoil events and nuclear recoil events with very high efficiency. As shown in Fig. 5, the F_{prompt} parameter, defined as the fraction of light in an argon scintillation pulse that arrives within the first 90 ns, is distinctly different in electron recoil events and nuclear recoil events. A cut on F_{prompt} was used to select the electron recoil events for the ^{39}Ar analysis, which was the only explicit cut applied to the data at KURF. The data acceptance in the F_{prompt} region from 0.05 to 0.55 was greater than 99% for energies above 50 keV_{ee}, with a very high rejection efficiency of nuclear recoil events.

4.2. Conservative ^{39}Ar Analysis

Fig. 6 shows the energy spectra taken with the underground argon during surface commissioning and at KURF. The atmospheric argon spectrum at KURF is also plotted for reference. The muon veto system was able to reduce the background rate by a factor of ~ 5 at surface, while the underground operation at KURF revealed a background reduction factor of ~ 25 without the muon veto. The cosmic ray muon rate at KURF was measured, using two of the muon veto panels stacked horizontally, to be $\sim 1 \mu/\text{m}^2/\text{min}$, which is approximately 10,000 times lower than that at surface. Due to the low muon rate, the muon veto had no noticeable effect on the underground argon data,

Figure 6: The energy spectra recorded in the argon detector under different conditions. Red: underground argon data at surface; purple: underground argon data at surface with an active cosmic ray veto; blue: underground argon data at KURF; green: atmospheric argon data at KURF.

and the veto cut was not applied in the analysis to avoid unnecessary dead time. A residual event rate of 20 mBq was observed in the 50-800 keV ^{39}Ar window in the measurement of underground argon at KURF.

Data of approximately 100 kg·hr were collected for both underground argon and atmospheric argon at KURF. A conservative upper limit on the ^{39}Ar content in the underground argon was obtained by ignoring the detector background and attributing all of the activity in the underground argon sample to ^{39}Ar . As illustrated in Fig. 7, the ratio of the event rate in underground argon to that in atmospheric argon as a function of energy shows that the best energy window to extract an ^{39}Ar upper limit is from 300 keV $_{ee}$ to 400 keV $_{ee}$. The residual event rate in this energy window in the underground argon data after applying the PSD cut was (1.87 ± 0.06) mBq. This is $(1.71 \pm 0.05)\%$ of the event rate in the atmospheric argon spectrum, and can be taken as a first estimate of the relative ^{39}Ar upper limit in underground argon compared to atmospheric. However, given that background events are included in both spectra and the underground argon data have a lower total rate than the atmospheric data, this estimate must be taken only as a conservative upper limit.

Figure 7: The ratio of the event rate in underground argon to that in atmospheric argon.

245 4.3. Background Subtraction Analysis

246 A more stringent limit on the abundance of ^{39}Ar in underground argon
 247 was obtained by subtracting from the observed underground argon spectrum
 248 the estimated events from known background radioactivity. The major back-
 249 ground components that were identified were due to the PMT, the PMT base,
 250 and the copper shielding. The Geant4 Monte Carlo simulation package [26]
 251 was used to estimate the background contribution from these sources. Back-
 252 ground contamination from an external source was also identified.

253 To evaluate the PMT background, three Hamamatsu R11065 PMTs and
 254 the electronic components for one PMT base were sent to the Gran Sasso
 255 Low Background Counting Facility [27] for radioactivity measurement. As
 256 illustrated in Tab. 1, the U and Th activities were measured at different
 257 points of their decay chains. A break in secular equilibrium was identified in
 258 the PMT ^{238}U measurement. As a result, the background contribution from
 259 the ^{238}U component of the PMT was simulated assuming different activities
 260 in the upper part and lower part of the chain. An additional 25% uncertainty
 261 was added to the analysis to account for the unknown position of radioactivity
 262 inside the PMT.

263 Background from the cosmogenic radioactivity in the copper shield was
 264 also estimated. The specific copper sample in the experiment was not counted;
 265 instead, equilibrium cosmogenic copper activation values, as reported in

Table 1: Measured radioactive activity in the major detector components.

Decay Chain	Measurement Point	PMT (mBq)	Base (mBq)	Cu (mBq/kg)
^{232}Th	^{228}Ra	6 ± 1	41 ± 2.8	-
	^{228}Th	6 ± 1	45 ± 4.7	-
^{238}U	^{234}Th	190 ± 40	25 ± 3.7	-
	^{234m}Pa	90 ± 40	< 149	-
	^{226}Ra	18 ± 1.2	32 ± 1.9	-
^{235}U	^{235}U	7 ± 1	1.4 ± 0.4	-
^{40}K	^{40}K	79 ± 11	65 ± 9.3	-
^{60}Co	^{60}Co	8.8 ± 0.8	< 1.2	2.1 ± 0.19
^{57}Co	^{57}Co	-	-	1.8 ± 0.4
^{58}Co	^{58}Co	-	-	1.7 ± 0.09
^{56}Co	^{56}Co	-	-	0.2 ± 0.03

Ref. [28] and as listed in Tab. 1, were used. The copper measured in the reference was exposed to cosmic rays at LNGS, Italy (altitude 985m above sea level), and the activities were scaled down by a factor of 2.1 to reflect the lower cosmic ray flux at sea level, as suggested by Ref. [28]. Our Geant4 simulation was used to translate the copper activities into detector background rates. A 25% uncertainty in this background rate was added in the later analysis to account for the uncertainties in the copper exposure history, the variations in the cosmic ray flux with latitude, and the (small) overburdens covering our copper during exposure.

While the backgrounds from the detector materials described above are expected to be identical in the measurements of atmospheric and underground argon, the presence of radioactive noble gas contaminants in the argon could produce a background signal that is different between the two measurements. The radon levels in the measurements were found to be negligible from both alpha studies and ^{214}Bi - ^{214}Po coincidence searches. In addition, the observed event rates were stable over time and the two measured energy spectra were consistent above the ^{39}Ar energy window, as illustrated in Fig. 7. Another radioactive noble gas is ^{85}Kr , an anthropogenic isotope with a beta decay endpoint energy of 687 keV, very close to that of ^{39}Ar .

285 The level of ^{85}Kr in the underground argon is expected to be extremely low
 286 because no efficient underground ^{85}Kr production mechanism is known. In
 287 any case, ^{85}Kr in the underground argon would be conservatively considered
 288 to be ^{39}Ar in the analysis. ^{85}Kr in the atmospheric argon reference sample,
 289 on the other hand, could artificially lower the apparent ^{39}Ar activity ratio
 290 between the underground and atmospheric argon samples. The krypton level
 291 in the high purity atmospheric argon purchased as our standard was mea-
 292 sured by the manufacturer to be less than 40 ppb. With a typical $^{85}\text{Kr}/\text{Kr}$
 293 ratio of 15 ppt, the ^{85}Kr decay rate in the reference sample would be less
 294 than 1.8% of the ^{39}Ar decay rate. A systematic uncertainty was added in the
 295 analysis to account for this potential effect.

296 Besides the intrinsic background in the detector, it was discovered that
 297 a weak ^{252}Cf source (~ 5000 n/s) used by another experiment at KURF
 298 contributed non-negligible background to the argon detector, even though it
 299 was stored 45 ft away. Removing the ^{252}Cf source from the lab reduced the
 300 underground argon event rate in the 300-400 keV_{ee} window by 40%, but only
 301 3 hours of ^{252}Cf -free data were collected because the detector was scheduled
 302 to shut down. To investigate this ^{252}Cf background contamination, another
 303 short run with the ^{252}Cf source right beside the detector (~ 2 ft) was taken,
 304 which provided a ^{252}Cf neutron source calibration spectrum.

305 The ^{252}Cf neutron background contamination spectrum (source at 45 ft) is
 306 shown in Fig. 8a, which was produced by subtracting the livetime-normalized
 307 energy spectrum of the ^{252}Cf -free data from the normalized spectrum with
 308 the ^{252}Cf source in its storage location. The ^{252}Cf source calibration spectrum
 309 (source at 2 ft) is also shown in Fig. 8a, with its amplitude scaled down to
 310 match the ^{252}Cf neutron background spectrum (source at 45 ft). The shapes
 311 of the two spectra are similar above 250 keV_{ee}, but are significantly different
 312 at lower energies.

313 The low energy difference between the two spectra in Fig. 8a is explained
 314 by inelastic scattering of fast ^{252}Cf neutrons on ^{19}F nuclei in the PTFE, which
 315 produces gamma rays at 110 keV_{ee} and 197 keV_{ee} following the excitation
 316 of ^{19}F nuclear energy levels. Signatures of the ^{19}F gamma rays were also
 317 observed in the measurements on surface, where high energy cosmogenic
 318 neutrons are prevalent, as can be seen in Fig. 6. The suppression of the ^{19}F
 319 gammas in the ^{252}Cf neutron background spectrum (source at 45 ft) indicates
 320 that the neutrons lose energy before reaching the detector and are less capable
 321 of exciting ^{19}F . On the contrary, as discussed below, the energy region above
 322 250 keV_{ee} is dominated by high energy gamma ray emission following the

Figure 8: (a) the measured energy spectra of electron recoil events induced by the ^{252}Cf neutron source at different distances from the argon detector: ^{252}Cf contamination spectrum (source at 45 ft) and ^{252}Cf calibration spectrum (source at 2 ft); (b) Monte Carlo simulated energy spectra induced by ^{252}Cf neutrons and by thermal neutrons generated right outside the detector shielding. The neutron calibration and simulation spectra have been scaled to match the ^{252}Cf background contamination spectrum above 250 keV_{ee}.

capture of neutrons in different detector components.

Monte Carlo simulations performed using Geant 4.9.6.p03 support the above explanations of the neutron spectra. Fig. 8b shows the simulated electron recoil spectra in the low background liquid argon detector induced by ^{252}Cf neutrons and by thermal neutrons generated right outside the detector shielding. Energy resolution equivalent to that in the ^{39}Ar measurement was applied, and the spectra were normalized to match Fig. 8a above 250 keV_{ee}. The simulations reproduced the low energy features induced by inelastic scattering of ^{252}Cf neutrons on ^{19}F in PTFE. It also confirmed that the spectral shape above 250 keV_{ee} does not depend significantly on the incoming neutron energy, or equivalently, on source position.

To account for the neutron contamination in the bulk of the data, we fitted the ^{252}Cf neutron background spectrum (source at 45 ft) to the ^{252}Cf source calibration spectrum (source at 2 ft) above 250 keV_{ee}, and used the fit result and uncertainty to estimate the ^{252}Cf background rate (source at 45 ft) in the energy region of interest. This method includes the uncertainty of the spectral shapes and improves the accuracy of the ^{252}Cf background rate estimation.

Table 2: The expected background rate in 300 - 400 keV_{ee} from different sources.

Source	²⁵² Cf	PMT	Base	Copper
Rate (mBq)	0.82 ± 0.16	0.29 ± 0.08	0.07 ± 0.02	0.36 ± 0.11

341 A summary of the expected background contributions in the 300 - 400 keV_{ee}
342 energy region of the low background detector measurement is shown in Tab. 2.
343 To be conservative, the contributions from detector components whose ra-
344 dioactivities were not specifically measured are not included in the back-
345 ground estimation. This includes, for example, the long lived radioisotopes
346 in the OFHC copper shielding, as well as any activity in the PTFE container;
347 at typical radioactivity levels reported by other authors, these contributions
348 would be small.

Figure 9: The background spectra expected from the identified sources of radioactivities compared to the observed spectrum. The rate excess around 100 keV_{ee} in the summed background is due to inelastic neutron scattering in the neutron calibration spectrum.

349 In addition to the statistical uncertainties in the activity measurements
350 listed in Tab. 1 and the systematic uncertainties discussed earlier, the PMT
351 and base background estimates in Tab. 2. include a 25% uncertainty to ac-

count for the unknown spatial distribution of the radioactive contaminants within the components. Additionally, we include a 5% uncertainty to account for approximations in the Monte Carlo geometry for all radioactivity simulations.

The total predicted background spectrum is shown in Fig. 9, together with the individual spectra from each of the components. The high statistics ^{252}Cf source calibration spectrum is scaled and used in place of the ^{252}Cf background spectrum (source at 45 ft). Above 200-250 keV_{ee}, the summed background spectrum looks similar to the observed one; the excess of events around 100-200 keV_{ee} compared to the observed spectrum is due to neutron inelastic scattering in the neutron calibration data, as discussed above.

Table 3: A summary of the background subtraction analysis. The entire upper limit ^{85}Kr rate is taken as an uncertainty in the background subtracted NAr rate. To convert these rates into activities per unit mass, an argon active mass of 0.56 ± 0.03 kg can be used.

	Rate/mBq, (300, 400) keV
Natural Ar (NAr)	108.78 ± 0.39
Underground Ar (UAr)	1.87 ± 0.06
Estimated Background	1.54 ± 0.22
^{85}Kr in NAr	< 1.83
NAr, Background Subtracted	107.2 ± 1.9
UAr, Background Subtracted	0.32 ± 0.23

The known background components account for 80% of the activity in the underground argon spectrum in 300 - 400 keV_{ee}. After subtracting the estimated backgrounds, a residual event rate of (0.32 ± 0.23) mBq remains in that energy region, as summarized in Tab. 3. From this we deduce a 95% C.L. upper limit of 0.65% on the ^{39}Ar activity in underground argon relative to that in atmospheric argon. Using the reported ^{39}Ar activity of (1.01 ± 0.08) Bq/kg in natural argon [5], we can similarly obtain a 95% C.L. upper limit of 6.6 mBq/kg on the specific ^{39}Ar activity in this underground argon sample.

372 5. Measurement of the Second Underground Argon Sample

373 The DarkSide-50 detector would be the first dark matter detector utilizing
 374 the low ^{39}Ar underground argon as the active volume. To confirm the low
 375 ^{39}Ar concentration in the batch processed underground argon [14, 20], a sub-
 376 kilogram sample (the second sample) was measured for ^{39}Ar radioactivity
 377 with the low background detector. This measurement took place in summer
 378 2012 and the difference from the previous measurement is summarized below.

- 379 1. The ^{252}Cf source was removed from the underground laboratory.
- 380 2. The R11065 PMT was replaced with a lower radioactivity model R11065-
 381 10 and the customized high voltage divider was upgraded to low-radioactivity,
 382 PTFE-based version utilizing surface-mount components.
- 383 3. The high-crystalline Teflon container was replaced with a Spectralon
 384 one in the hope of increasing light yield.

Figure 10: Left: Mass-normalized energy spectra observed in the first and second underground argon samples. Right: The alpha-like (high F_{prompt} , $>1000 \text{ keV}_{ee}$) event rate and electron-like (low F_{prompt} , $300\text{--}800 \text{ keV}_{ee}$) event rate measured in the second underground argon sample.

385 Unexpectedly, the event rate in the second sample was found to be higher
 386 than that in the 2011 measurement using the first sample, as shown in Fig. 10
 387 (left). Because the higher rate was also observed at energy levels above
 388 the ^{39}Ar end point, it was not interpreted as an increase of ^{39}Ar content
 389 in the second sample. Further analysis of this data showed that the event
 390 rate decreased over time, as shown in Fig. 10 (right). The gamma/electron
 391 event rate between 300 keV_{ee} and 800 keV_{ee} decreased by $\sim 30\%$ over 80 hrs,

392 and the alpha-like event rate dropped by 50%. By contrast, the event rate
 393 in the measurement of the first sample was very stable over time. It is
 394 suspected that the additional background in the second sample was due to
 395 radon contamination although the statistics of the acquired data were not
 396 adequate to measure the half life of the rate decay.

397 A simple rate analysis without background subtraction yielded an up-
 398 per limit of 2.0% on the ^{39}Ar concentration in the second underground ar-
 399 gon sample relative to atmospheric, compared to the 1.8% result from the
 400 first sample. If the decreasing background component in the second sam-
 401 ple is attributed to radon, and the radon rate inferred from the observed
 402 decrease is subtracted, the relative ^{39}Ar upper limit can be brought down
 403 to $\sim 1\%$. Due to the significant uncertainty from the radon contamination,
 404 background subtraction analysis was not performed on this sample. We ex-
 405 pect the DarkSide-50 detector to provide a more sensitive measurement of
 406 the ^{39}Ar activity in this batch of underground argon in its 2015 operation.

407 6. Mantle Origin Hypothesis for the Underground Argon

408 The extraordinarily low ^{39}Ar content in the underground argon gas ex-
 409 tracted from the Doe Canyon field suggests that this argon originates from
 410 the Earth’s mantle, instead of from the crust where the ^{39}Ar content has
 411 been found to be relatively high [6, 7, 8]. Further support of this hypothesis
 412 can be obtained from the study of stable argon isotope ratios [11, 12, 13].

413 Atmospheric argon has a ratio of $^{40}\text{Ar}/^{36}\text{Ar}$ of 295.5 [29], whereas Mid
 414 Ocean Ridge Basalts, which were derived by partial melting of the upper
 415 mantle, have measured $^{40}\text{Ar}/^{36}\text{Ar}$ ratios of 296 to 40,000 [30, 31]. The large
 416 argon isotopic variability in the basalts reflects mixing between the upper
 417 mantle argon, which has a $^{40}\text{Ar}/^{36}\text{Ar}$ value around 41,000, and atmospheric
 418 argon introduced into the basalts upon eruption onto the seafloor. By com-
 419 parison, the $^{40}\text{Ar}/^{36}\text{Ar}$ ratio for argon from the Doe Canyon CO_2 gas well
 420 was measured to be 13,300 using a SRS UGA 300 residual gas analyzer, very
 421 close to the mantle values. By contrast, the argon from the National Helium
 422 Reserve [9] had a measured $^{40}\text{Ar}/^{36}\text{Ar}$ ratio of 1,640, which is between at-
 423 mospheric and mantle values. The low ^{39}Ar limit for the National Helium
 424 Reserve compared to expected levels from the crust, and the intermediate
 425 value of the $^{40}\text{Ar}/^{36}\text{Ar}$ ratio may suggest that the source of the gas is deeper
 426 than the crust. The argon from the National Helium Reserve was separated
 427 from natural gas that is expected to be biotic, and therefore crustal in origin;

428 however, noble gases in crustal fluids can show a mantle signature, particu-
 429 larly in regions that may be undergoing tectonic extension [32]. It should also
 430 be noted that there is an alternative hypothesis for a deep origin of natural
 431 gas [33].

432 7. Conclusion

433 We developed a low background, single phase, liquid argon detector to
 434 measure the ^{39}Ar activity in argon obtained from underground sources. The
 435 background rate in the detector when operated in the KURF underground
 436 laboratory was $<4\text{ mHz/kg}$ in the $300\text{--}400\text{ keV}_{ee}$ energy range. We obtained
 437 an upper limit of 0.65% on the ^{39}Ar activity in the first argon gas sample
 438 extracted from the Doe Canyon field in Cortez, Colorado, relative to atmo-
 439 spheric argon, that is, 6.6 mBq/kg specific ^{39}Ar activity. This limit is almost
 440 10 times lower than earlier results [9] and, to the best of our knowledge,
 441 demonstrates the highest sensitivity to ^{39}Ar in argon yet obtained. A follow-
 442 up measurement using a second underground argon sample confirmed that
 443 the ^{39}Ar content has remained low with a similar but slightly higher limit.

444 This result represents an important milestone in argon-based direct detec-
 445 tion dark matter searches, as at this activity multi-ton two-phase detectors
 446 can be operated without pileup. The large reduction in ^{39}Ar activity will also
 447 allow current and next-generation experiments using underground argon to
 448 operate with lower threshold energies than experiments using atmospheric
 449 argon. This will improve the sensitivity of argon experiments, especially in
 450 the low mass WIMP region. Detailed discussion on the impacts of this work
 451 on argon-based rare events detection can be found in [19].

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