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$^{39}Ar/Ar$ measurements using ultra-low background proportional counters

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HIGHLIGHTS

- $^{39}Ar/Ar$ age dating is important for understanding environmental water migration.
- Ultra low background proportional counters have been developed.
- ^{39}Ar is detected in atmospheric argon at a rate of 70.3 counts per day. The demonstrated background is 166 counts per day.
- Age dating is possible for water with underground residence time of up to 1000 years.

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ABSTRACT

Age-dating groundwater and seawater using the $^{39}Ar/Ar$ ratio is an important tool to understand water mass-flow rates and mean residence time. Low-background proportional counters developed at Pacific Northwest National Laboratory use mixtures of argon and methane as counting gas. We demonstrate sensitivity to ^{39}Ar by comparing geological (ancient) argon recovered from a carbon dioxide gas well and commercial argon. The demonstrated sensitivity to the $^{39}Ar/Ar$ ratio is sufficient to date water masses as old as 1000 years.

1. Introduction

Argon-39 is an important tracer in environmental age dating of glaciers, oceans, and groundwater (Loosli, 1983; Loosli and Purtschert 2005). The 269-year half-life of ^{39}Ar allows dating in the challenging age range between methods that are applicable for samples as old as ~50 years (^{3}H, $^{3}H/^{3}He$, ^{85}Kr, CFCs, SF_6) and methods applicable for samples older than 1000 years (^{14}C, ^{36}Cl, ^{81}Kr). This intermediate age range, 50–1000 years, is important for characterizing the flow of groundwater (Corcho Alvarado et al., 2007, Newman et al., 2010, Visser et al., 2013). Argon-39 is almost exclusively produced by cosmic-ray interactions and production by man in the atomic age is negligible(Cennini et al., 1995). Additionally, the $^{39}Ar/Ar$ ratio is used so quantitative argon yields from the water are not required and details about the recharge process do not influence the dating results in contrast to other methods. This lends an inherent robustness to ^{39}Ar age dating and facilitates quantification of water migration and climate history (Corcho Alvarado et al., 2011). Despite the utility of ^{39}Ar age dating, the required sensitivity for direct beta counting is challenging and the only laboratory to develop relevant sensitivities is the underground laboratory in Bern (Loosli et al., 1986). Sensitivity to ^{39}Ar has been demonstrated using atom trap trace analysis and atomic mass spectroscopy (Jiang et al., 2011).

Ultra-low-background proportional counters (ULBPCs) have been developed at Pacific Northwest National Laboratory (PNNL) (Aalseth et al., 2009). These counters are designed to measure radioactive isotopes from environmental samples including ^{3}H, ^{14}C, ^{37}Ar, and ^{39}Ar. After installation in an ultra-low-background counting system (ULBCS) at the PNNL Shallow Underground Laboratory, the ULBPCs have been shown to have a count rate of 234 counts per day (cpd) in the energy range 3–400 keV when filled with 7 atm of P-10 counting gas, 90% Ar–10% CH_4 (Seifert et al., (2013)).

Atmospheric argon is predominantly composed of ^{40}Ar; however, trace amounts of ^{39}Ar are found in the atmosphere. Argon-39 decays to ^{39}K via beta decay with a Q-value of 565 keV and a half-

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life of 269 years. The activity of atmospheric argon is 1.01 Bq/kg, corresponding to an abundance of 0.808 ppq (Benetti et al., 2007). The ULBPCs at PNNL have an internal volume of 100 mL and are designed to run with pressures up to 10 atm. Commercial P-10 gas (90% Ar, 10% CH_4) prepared with atmospheric-sourced argon thus provides 14.0 disintegrations per day of ^{39}Ar activity for each atmosphere of fill pressure at 297 K. With a 3-keV low-energy threshold and a 7-atm fill pressure, ULBPC efficiency for ^{39}Ar is estimated to be 85%. Thus the observed rate under these conditions with commercial P-10 gas of 234 cpd is expected to include 83.3 cpd from the ^{39}Ar activity, roughly one-third of the observed rate.

Argon-39 is created in the atmosphere by cosmic-ray interactions producing fast neutrons driving the ^{40}Ar(n,2n)^{39}Ar reaction. Although ^{39}Ar can be created underground through the reaction ^{39}K(n,p)^{39}Ar (Yokochi et al., 2012), gas sourced from an appropriate geological depth and composition has been found to be low in ^{39}Ar activity (Acosta-Kane et al., 2008). Extraction of low-activity argon from a carbon dioxide well in Colorado has recently been developed as a resource for rare-event searches such as direct detection of dark matter (Back et al., 2012). Experimental efforts have not measured any ^{39}Ar radioactivity in the argon from this CO_2 well, the best limit is currently 0.65% the radioactivity of atmospheric argon (Xu et al., 2012). This manuscript describes results from filling a ULBPC at PNNL with this geological argon.

In this work, ULBPC measurements were made on argon from two sources, one referred to as geologic argon and one referred to as atmospheric argon. The measurements were made with a single ULBPC. The geologic argon was extracted from a CO_2 gas stream from a southwestern Colorado well by a vacuum-swing pressure-absorption process. The extracted gas mixture, a mixture of helium, nitrogen and argon, was transported to the Fermi National Accelerator Laboratory and purified in a cryogenic distillation column (Back et al., 2012). The atmospheric argon sample was commercial detector grade P10 gas with argon distilled from air.

Counting these argon samples permits measurement of ULBPC with and without atmospheric ^{39}Ar activity allowing a demonstration of the sensitivity for age dating using ^{39}Ar/Ar ratios. Additionally, the lower background levels observed with geologic argon are relevant for improving sensitivity for ^{3}H and ^{14}C samples prepared as methane, where geologic argon can be used for the remainder of the required count gas in an ULBPC.

2. Proportional counter/experimental description

The ULBPC technology developed over the past several years by PNNL is the product of an effort to produce a low-background, physically robust, gas-proportional counter for low-level counting of gas samples. The ULBPC was designed to handle a wide range of gas volumes and has high beta detection efficiency. The materials chosen for the detector were selected for their radiopurity. High-purity electroformed copper offers low radioactivity along with good electrical and mechanical properties. The ULBPC body is an electroformed copper cylinder roughly 9 in. in length having a ~0.1 L internal volume. PCTFE (polychlorotrifluoroethylene), was chosen for the gas seal and high-voltage insulation for its low gas permeability and reasonable measured radioactivity. The ULBPC anode wire is 0.001-in.-diameter niobium.

A shallow underground laboratory was recently constructed at PNNL in Richland, Washington (Aalseth et al., 2012). This facility, commissioned in late 2010, supports the dual objectives of performing ultra-sensitive measurements and providing ultra-clean materials and radiation detector research. The shallow underground facility has an effective depth of ~30 m water-equivalent.

After the ULBPC was filled with a gas sample above ground, it was moved to the shallow underground laboratory and placed in the ULBCS. The ULBCS is designed with both active and passive shielding around the detectors (Seifert et al., 2013). The passive layers of shielding include approximately 3 in. of copper around the core measurement chamber that houses the detectors, 6 in. of lead around the copper, and an additional outer layer of 1 in. of 30%-borated polyethylene for neutron shielding. This passive shielding is surrounded by active cosmic-ray veto shielding in the form of 2-in.-thick polyvinyl toluene scintillator paddles. The signal path in the ULBCS cave has been optimized to reduce micro-discharge events (Mace et al., 2013).

The count gas composition loaded into the ULBPC detector was 90% Ar, 10% CH_4, with a partial pressure of 6.3 atm of argon and a total fill pressure of 7 atm. After the detector was installed in the ULBCS cave, an ^{241}Am source (~40 μ Ci) was placed on the detector and high-voltage bias applied. The high-voltage bias on the ULBPC detector was adjusted, near 3250 V for this type of load, such that the gamma-ray peak of 59.5 keV from the ^{241}Am source was centered at a specific channel (nominally channel 10,405 of 65,536) to optimize the dynamic range for an energy range of 0–400 keV. The resulting calibration peak is shown in Fig. 1. After energy calibration data were collected and the ^{241}Am source was removed, the detector counted the gas sample. The geologic argon was counted in two separate ULBPC fills, one for 77.7 days (live time of the detector) and one for 120 live days, in the ULBCS cave. The atmospheric argon was measured for 45.4 live days. All three fills were performed with the same proportional counter.

The system stability was found to be excellent over these time periods. Fluctuations in the counting rates were found to be consistent with the expected statistical fluctuations over the 100 day periods. The system calibration is now done weekly and the gain variation is less than 1% per week.

The data collected from the argon measurements were analyzed using pulse-shape discrimination to examine each digitized pulse in the data set (Aalseth et al., 2013). The differential pulse-height spectrum in the energy range 0–400 keV is shown for one

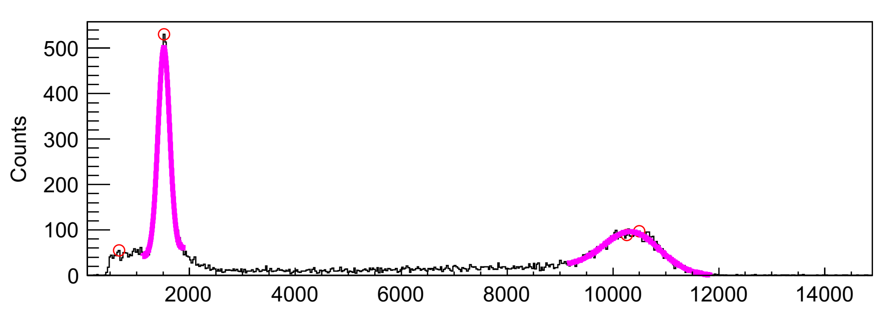

Fig. 1. Calibration spectra from ^{241}Am source with a Gaussian fit to the 59.5 keV peak. The induced copper x-ray peak at 8.0 keV is also fit with a Gaussian. The resolution (FWHM) is 17% at 8.0 keV and 12% at 59.5 keV.