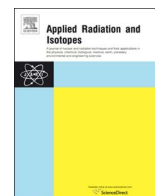




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Methods for using argon-39 to age-date groundwater using ultra-low-background proportional counting

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ABSTRACT

Argon-39 can be used as a tracer for age-dating glaciers, oceans, and more recently, groundwater. With a half-life of 269 years, ³⁹Ar fills an intermediate age range gap (50–1,000 years) not currently covered by other common groundwater tracers. Therefore, adding this tracer to the data suite for groundwater studies provides an important tool for improving our understanding of groundwater systems. We present the methods employed for arriving at an age-date for a given sample of argon degassed from groundwater.

1. Introduction

Recent concerns over climate change and water security have increased the need for understanding and developing best practices for groundwater resource management. One important component of understanding groundwater flow systems and groundwater resource sustainability is identifying the age of groundwater. Groundwater age has been used in the field of hydrogeology for many years (Kazemi et al., 2006), but the meaning of groundwater age and the methods for determining it have evolved. Early on, researchers assumed a uniform age for all pore water at a specific location of the aquifer (Plummer, 2005), providing an age estimate based on a single tracer. However, in some cases, when the same groundwater has been age-dated with multiple tracers, the age estimates have been observed to be different (Lehmann et al., 2003; Bruce et al., 2007; Troldborg et al., 2008; Massoudieh and Ginn, 2011). More recently it has been suggested that groundwater age should be considered and assessed as a distribution rather than as having a single mean age (Bethke and Johnson, 2008; Massoudieh et al., 2012; Massoudieh, 2013; McCallum et al., 2014). Therefore, a common approach is to use a suite of tracers (called a multi-tracer approach) to determine the groundwater age distribution. Applications of these multi-tracer studies range from estimation of recharge rates (McMahon et al., 2011) to the calibration of groundwater flow models (e.g., Reilly et al., 1994; Szabo et al., 1996; Portniaguine and Solomon, 1998; Ginn et al., 2009), to understanding the transport of contaminants (Böhlke and Denver, 1995; Bethke et al.,

2000; Visser et al., 2015), to assessing aquifer and production well vulnerability (Visser et al., 2013; Åkesson et al., 2015).

Currently, the common tracers used for dating groundwater are ³H for young water (< 50 yrs) and ¹⁴C for old water (> 1000 yrs). Adding an intermediate age tracer provides groundwater scientists with the ability to better constrain groundwater age distributions that are used for determining aquifer sustainability and vulnerability to contamination (Corcho Alvarado et al., 2007; Visser et al., 2015). Pacific Northwest National Laboratory (PNNL) has collected groundwater samples in collaboration with the United States Geological Survey (USGS) in California in order to add ³⁹Ar as an additional tracer for age-dating groundwater in the Central Valley Aquifer System.

2. Sampling

Groundwater samples were collected in Fresno, California in September 2014 from three wells (180-1, 180-2, 170). Two additional groundwater-sampling campaigns were conducted in 2015 and 2016, also for wells in the Central Valley Aquifer System in California. Prior to collecting the groundwater samples, the wells were purged until the pH, specific conductance, and temperature had stabilized. Dissolved gasses were then extracted from the groundwater using a degasification system that uses a Liquicel membrane contactor.

Fig. 1a shows the sampling apparatus used at one of the California groundwater collection sites. Fig. 1b shows a flow diagram of the sampling apparatus. Water flows from the well through the membrane

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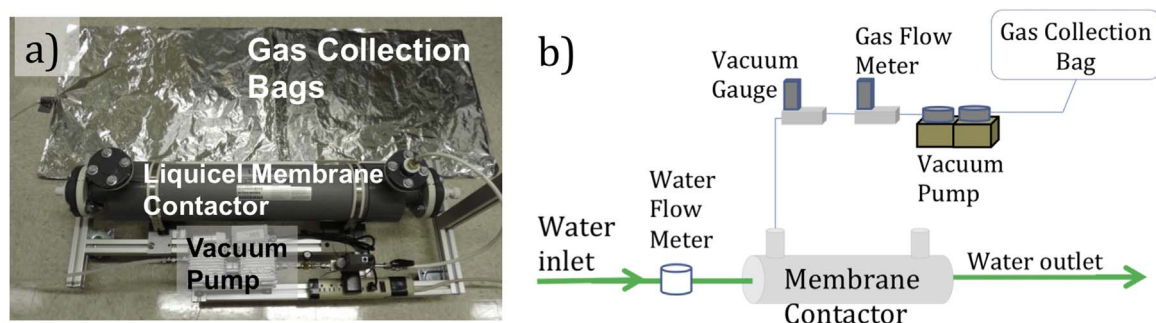


Fig. 1. Groundwater degasification system diagram.

contactor via a hose and then to an approved disposal area via a hose attached to the membrane outlet. A vacuum pump is connected to the gas side of the membrane, and the output of the vacuum pump is attached to a Tedlar gas sample bag. Running the vacuum pump to remove any atmospheric air (modern ^{39}Ar) from the system purges the membrane contactor before gas is collected in the sample bag. After this purge process, a new sample bag is attached to the outlet line of the vacuum pump. The amount of gas sample needed for each measurement is around 200 L; however, around 300 L of gas were collected from the Fresno wells to compensate for losses during separation, purification, and detector loading. Collection of this volume of gas requires degasification of ~3000–5000 gallons of groundwater. Depending on the flow rate at the sampling point, this sample collection can take 5–8 h. Water on the outlet side of the membrane is disposed of in a manner consistent with the purge water practices of that well.

One of the concerns with this process was the possibility of argon diffusing into the gas collection bags during transport and storage, thereby contaminating the sample gas with atmospheric argon. To investigate this, a diffusion experiment was conducted on a set of gas collection bags. A sample bag was filled with nitrogen, oxygen, and argon, with concentrations being 2–3 orders of magnitude lower than atmospheric concentrations. A mass spectrometer was used to measure the gas composition inside the bag at four intervals over a 29-day period. The change in gas composition measured with the mass spectrometer was compared to atmospheric concentrations to calculate the amount of contamination. The results of this experiment showed an argon contamination of 0.8% and an oxygen contamination of 2.3% at 29 days. The gas samples collected in this study were transferred back to PNNL and processed in less than 1 week, so the argon contamination due to transport and storage in the gas sample bags was estimated to be less than 0.2%. The sampling and collection methods have been improved for the more recent sampling campaigns so that under the current procedure, the gas is collected in a gas collection bag and then transferred to a compressed gas cylinder in the field prior to shipment to PNNL.

3. Sample chemistry argon purification

3.1. Separation and purification

At the laboratory, the argon was extracted from the degassed groundwater samples using PNNL's argon separation and purification bench. The gas flow diagram was published previously (Aalseth et al., 2016). The first step in the argon separation process is to remove nitrogen from the sample using a custom-designed pressure swing adsorption (PSA) system. This custom PSA system was designed to maximize argon recovery from the sample gas. The PSA separation process produces a product consisting of 5–6% argon in oxygen, with an argon recovery greater than 85%. Atmospheric contamination from the gas separation process has been demonstrated to be less than 1%. After the oxygen and argon have been separated from the gas sample using the PSA process, oxygen is then removed by reacting oxygen with

hydrogen on a platinum catalyst. This combustion process is followed by several clean up steps that remove water, helium, hydrogen, and residual nitrogen, resulting in a sample of pure argon.

3.2. Detector loading

The last step in the process is to load the purified argon into an ultra-low-background proportional counter (ULBPC) (Aalseth et al., 2009). Methane, used as a quench gas, is added to the detector with the argon sample, such that the resulting gas mixture contains 10% methane and 90% argon (P10). The detector is then taken to PNNL's Shallow Underground Laboratory (Aalseth et al., 2012) and counted in the low-background counting system (Seifert et al., 2013).

4. Detector calibration

Prior to measuring groundwater samples for ^{39}Ar , each ULBPC is characterized at a specific pressure (10 atm) and count gas blend (P10) by collecting modern argon (atmospheric argon) and geologic argon (^{39}Ar -free) reference spectra.

4.1. Modern argon

Modern argon is extracted from the atmosphere for use in commercially available P10 gas. Ultra-pure modern argon P10 was counted in a proportional counter as a reference for 100% modern argon (or 100 pMar).

4.2. Geologic argon

Geologic argon was extracted from a CO_2 well in southwestern Colorado using a vacuum-swing pressure adsorption process. The gas sample from the CO_2 well (a mix of helium, nitrogen and argon) was sent to Fermi National Accelerator Laboratory and purified in a cryogenic distillation column (Back et al., 2012). The pure geologic argon was counted in a proportional counter together with methane (count gas blend P10). Since the geologic argon sample is free from ^{39}Ar , the measured counts from this geologic argon sample are due only to the detector background.

5. Measurement of ^{39}Ar

5.1. Sample analysis

A groundwater sample is analyzed by comparing the sample histogram to the modern and geologic reference data (Fig. 2). For a groundwater sample that is older than modern argon, the spectra will fall between the modern (red hash) and geologic (blue hash) argon reference spectra as shown in Fig. 2. Also illustrated in Fig. 2 is the net sample spectrum (green dots) calculated by subtracting the sample and the geologic argon detector background. The resulting spectrum is the ^{39}Ar beta-decay shape as measured in a ULBPC.

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