

Tracer Applications of Noble Gas Radionuclides in the Geosciences

October 09, 2012

Table of Contents

1. Summary
2. Noble Gas Radionuclides
3. Atom Trap Trace Analysis
4. Sampling
 - 4.1. Sample Collection
 - 4.2. Sample Preparation
5. Applications in the Geosciences
 - 5.1. Groundwater Residence Time
 - 5.2. Ocean Ventilation
 - 5.3. Ancient Glacial Ice
 - 5.4. Fluid Residence and Migration in the Crust

References

Appendix A. List of participants

Appendix B. Workshop agenda

1. Summary

The first *International Workshop on Tracer Applications of Noble Gas Radionuclides in the Geosciences* (TANGR2012) was held at Argonne National Laboratory on June 20-22, 2012, with support from the National Science Foundation, Argonne, and the University of Illinois at Chicago. This workshop was organized in response to recent developments in Atom Trap Trace Analysis (ATTA) that have enabled routine measurements of ultra-low concentrations of noble gas radionuclides in samples of water, ice, and gas. The workshop examined progress in ATTA, as well as applications of noble gas radionuclides to compelling scientific problems in the fields of hydrology, oceanography, glaciology, and other areas of the geosciences.

The organizers of the workshop are:

Zheng-Tian Lu, Argonne National Laboratory

Peter Schlosser, Lamont-Doherty Earth Observatory, Columbia University

William Smethie, Lamont-Doherty Earth Observatory, Columbia University

Neil Sturchio, University of Illinois at Chicago

The discussion topics and conveners are:

ATTA techniques – Zheng-Tian Lu, Argonne National Laboratory

Sample collection and purification – Neil Sturchio, University of Illinois at Chicago

Groundwater – D. Kip Solomon, University of Utah

Oceans – Toste Tanhua, University of Keil

Glaciers – Jeffrey Severinghaus, Scripps Institution of Oceanography

Volcanic/geothermal – B. Mack Kennedy, Lawrence Berkeley National Laboratory

A list of TANGR2012 participants and the workshop agenda are attached as Appendices A and B, respectively. Presentations from the workshop are available at the following website: <http://www.phy.anl.gov/events/tangr2012/>. This report summarizes the discussions that took place both during and after TANGR2012 about measurement techniques and applications of noble gas radionuclides in the geosciences.

The noble gas radionuclides ^{81}Kr (half-life = 229,000 yr), ^{85}Kr (10.8 yr), and ^{39}Ar (269 yr) have near ideal chemical and physical properties for tracing fluid transport in Earth systems. In practice, however, few studies have employed noble gas radionuclides because of the large sample sizes and the complex analytical systems required for measuring their extremely low isotopic abundances (10^{-16} – 10^{-11}). Most published studies have used low-level radioactive decay counting for ^{39}Ar and ^{85}Kr , but the low activity of ^{81}Kr has necessitated the development of various atom-counting methods over the past four decades.

The advent of ATTA as a new tool for routine measurements of rare noble gas isotopes has reignited the discussion among Earth scientists about how to best apply ATTA to compelling scientific problems. In this spirit TANGR2012 attendees considered this topic for two days and reached consensus on some important issues. We would like to make the following recommendations to the geoscience community and potential funding agencies:

Recommendations

1. We recommend the establishment of a dedicated ATTA facility, with separate instrumentation for routine measurements and for research dedicated to the further development of ATTA method. The size and shape of such a facility would be dictated by the projected evolution of the ATTA technology, which currently allows 120 measurements of ^{81}Kr and ^{85}Kr per atom trap per year. An ATTA facility could be designed with multiple atom traps to optimize its efficiency and versatility.
2. We recommend additional work to optimize sample collection and purification methods. In particular, we feel that a standard design for a robust, portable gas extraction apparatus should be developed, along with a standard design for a separation line for purification of Kr and Ar from extracted gas samples. Sample collection and purification protocols should be optimized for ATTA-3 sample-size requirements.
3. We recommend optimization of sampling strategies for noble gas radioisotopes on the basis of known properties of the study domain. Due to the large effort involved in such measurements some systems have been under sampled leading to ambiguities in the interpretation of the data. Increased capacity should help accommodate the increased sample load expected from optimized sampling plans.

These actions will better enable progress in the pursuit of scientific applications of noble gas radionuclides in the geosciences. Principal scientific thrusts of an ATTA facility would likely include surveys of groundwater residence times using ^{81}Kr , ^{85}Kr , and ^{39}Ar , age distributions of glacial ice using ^{81}Kr , and a survey of ^{39}Ar in the main water masses of the oceans to estimate circulation pathways, which in turn will place better constraints on circulation models. Other scientific questions involving deeper circulation of fluids in the Earth's crust and mantle are also within the scope of future applications.

This report is structured as follows: After a brief overview in Section 2 of the relevant noble gas radionuclides, Section 3 describes the ATTA method, and the ATTA-3 instrument capable of measuring both $^{81}\text{Kr}/\text{Kr}$ and $^{85}\text{Kr}/\text{Kr}$ ratios of environmental samples in the range of $10^{-14} - 10^{-10}$. For ^{81}Kr -dating in the age range of 150 kyr – 1,500 kyr, the required sample size is 5 – 10 micro-L STP of krypton gas, which can be extracted from approximately 100 – 200 kg of water or 40 – 80 kg of ice. For ^{85}Kr -dating of young groundwater, the required sample size is generally a factor of 10 less. At present, the laboratory at Argonne has one atom trap in operation and can analyze 120 samples per year. The same instrument has also been used to measure $^{39}\text{Ar}/\text{Ar}$ ratios of environmental samples down to the 1×10^{-16} level. However, the counting rate of ^{39}Ar needs to be improved by a factor of 10 – 100 before practical ^{39}Ar -dating can be realized.

Section 4 describes the methods for noble gas sample collection (Sec. 4.1) and purification (Sec. 4.2) required for Ar and Kr isotope measurements using the ATTA technique. Gas extraction is performed in the field using two types of apparatus: vacuum cylinder and membrane extractor, both having extraction efficiencies of 80-90%. Concentration and purification of Ar and Kr from the bulk extracted gas is done in laboratory employing an array of techniques including cryogenic distillation, adsorption on molecular sieves and activated carbon, gas chromatography, and gettering.

Section 5.1 discusses applications of ^{85}Kr , ^{39}Ar and ^{81}Kr in hydrology. Measurements in groundwater have given new insights into the behavior of aquifer systems. In particular, ATTA measurements of ^{81}Kr in the Nubian Aquifer of Africa, the Great Artesian Basin of Australia, and the Guarani Aquifer of South America have transformed our understanding of the long-term behavior of these large systems, allowing improved calibration and validation of numerical hydrodynamic models as well as cross-validation with other tracers (^4He and ^{36}Cl). With further dedicated development of ATTA, ^{39}Ar will become a standard tool in the evaluation of groundwater resources, particularly because it addresses a critical time range (100-1,000 yr) presently not well resolved by other tracers. ^{85}Kr is now routinely measured by ATTA and provides a valuable alternative to tritium- ^3He , chlorofluorocarbons, and SF_6 as a residence-time tracer for young (<60 yr), shallow groundwater that are most susceptible to contamination. When combined with other tracers, ^{85}Kr will improve the quality and reliability of groundwater flow and vulnerability assessments. Based on the present demand for complementary tracers, we conservatively estimate the demand for $^{81,85}\text{Kr}$ analysis by the U.S. hydrology community to be at least 1000 samples per year.

Section 5.2 discusses applications of ^{39}Ar in oceanography. Using low-level decay counting, $^{39}\text{Ar}/\text{Ar}$ measurements have previously been done for a limited number of samples from the oceans. These demonstrated the clear potential of ^{39}Ar to provide better resolution of ocean ventilation, pathways and mean residence times of the principal water masses. ^{39}Ar as a tracer

has a number of advantages: The half-life of ^{39}Ar , 269 yr, is well matched to the turnover time of the ocean; it does not have the reservoir effect of ^{14}C . Combination of ^{39}Ar and ^{14}C will provide better constraints on circulation models and climate history. A systematic survey of ^{39}Ar throughout the oceans will fill major gaps in our knowledge of deep ocean circulation and mixing, and will allow better predictions of oceanic sequestration of atmospheric CO_2 . Sampling of roughly 1000 samples in the Pacific Ocean, 500 in the Indian Ocean, 200 in the Arctic Ocean and 300 repeat samples in the Atlantic Ocean would provide a reasonable one-time coverage. This adds up to a demand for measurement of ~ 2000 new samples and 1000 archived samples.

Section 5.3 discusses applications of ^{81}Kr in glaciology. Polar ice cores have been used to reconstruct Earth's past climate and atmospheric composition as far back as 800 kyr in time. ^{81}Kr could potentially be used for dating of old ice with ages ranging from 100 kyr – 1,500 kyr. Old ice can be obtained not only from deep ice cores, but also at ice margins and Antarctic blue ice areas where it is being re-exposed by ablation. For paleoclimate studies this provides an interesting alternative to ice coring. An experiment is being carried out to use the well-dated stratigraphy of Taylor Glacier to test the feasibility and accuracy of ^{81}Kr -dating of old ice.

Section 5.4 discusses applications of noble gas isotopes in volcanic and geothermal systems. Determining the origin of crustal fluids and the time scales of fluid transport are essential for understanding the geochemical cycles of elements, as well as risk and resource management. The fluid migration rate or storage time in crustal reservoirs has rarely been determined due to the lack of optimal tracers. The ability to routinely analyze crustal fluid samples for noble gas radionuclides (^{39}Ar , ^{81}Kr and ^{85}Kr) will provide an indispensable tool for deriving a thorough understanding of the origin, evolution and migration of crustal fluids, such as in geothermal, CO_2 , and hydrocarbon reservoirs.

2. Noble Gas Radionuclides

There are three long-lived ($t_{1/2} > 1$ yr) noble-gas radionuclides with tracer applications in the environment: ^{81}Kr ($t_{1/2} = 230,000$ yr), ^{85}Kr (10.8 yr), and ^{39}Ar (269 yr). Being chemically inert, these three nuclides predominantly reside in the atmosphere. They follow relatively simple mixing and transport processes in the environment, and they can be extracted from large quantities of water or ice for analysis. These geophysical and geochemical properties are favorable for the purpose of radio-isotope dating (Collon *et al.*, 2004). The half-lives of the three tracer nuclides have different orders of magnitude, allowing them to cover a wide range of ages (Fig. 1).

^{81}Kr is a cosmogenic nuclide with an atmospheric $^{81}\text{Kr}/\text{Kr}$ ratio of $(5.2 \pm 0.4) \times 10^{-13}$ (Collon *et al.*, 1997). It has a long residence time and a spatially homogeneous distribution in the atmosphere, making it a desirable tracer for its dating range (Loosli and Oeschger, 1969). Compared to atmospheric production of ^{81}Kr , contributions from both spontaneous and neutron-induced fission are negligible because ^{81}Kr is shielded by ^{81}Br from the fission yields on the neutron-rich side (Lehmann *et al.*, 1993). At present, ATTA is the only method capable of measuring $^{81}\text{Kr}/\text{Kr}$ in environmental samples. The required sample size for a typical analysis is 100 – 200 L of water or 40 – 80 kg of ice.

^{85}Kr is amply produced during fission in nuclear reactors, and is released into the atmosphere due to reprocessing of spent nuclear fuel rods. The atmospheric $^{85}\text{Kr}/\text{Kr}$ ratio is approximately 2×10^{-11} . Due to its relatively short half-life, the spatial distribution of ^{85}Kr in the atmosphere is not as uniform as that of ^{39}Ar or ^{81}Kr . For example, $^{85}\text{Kr}/\text{Kr}$ in the northern hemisphere, where most of the nuclear fuel reprocessing plants reside, can be $\sim 20\%$ higher than that in the southern hemisphere, depending on the emission rate in the northern hemisphere (Weiss *et al.*, 1989). ^{85}Kr is useful for dating young (< 50 yr) groundwater (Smethie *et al.*, 1992; Althaus *et al.*, 2009; Momoshima *et al.*, 2011). At present, both Low-Level Decay Counting (LLC) and ATTA can measure ^{85}Kr in environmental samples. The results from the two methods agree in comparison studies.

^{39}Ar conveniently fills an apparent age gap (Fig. 1) between ^{85}Kr and $^3\text{H}/^3\text{He}$ on the shorter and ^{14}C on the longer time scale. This makes ^{39}Ar a much desired isotope for dating environmental samples on the time scale of a few hundred years (Loosli and Oeschger, 1968; Lehmann and Purtschert, 1997). Atmospheric ^{39}Ar is of cosmogenic origin with a $^{39}\text{Ar}/\text{Ar}$ ratio of 8×10^{-16} . There can be substantial subsurface production in granite rocks through the $^{39}\text{K}(n, p)^{39}\text{Ar}$ reaction and muon capture on ^{39}K (Lehmann *et al.*, 1993; Mei *et al.*, 2010). This effect should be evaluated in ^{39}Ar -dating of groundwater, particularly in geothermal systems or fractured crystalline rocks. In situ production of ^{39}Ar is not significant for dating ocean water. At present, LLC is used for ^{39}Ar analysis, but it requires several tons of water per sample. The ATTA-3 instrument has been used to measure $^{39}\text{Ar}/\text{Ar}$ in environmental samples on much smaller amounts of Ar than those required for LLC. However, the atom counting rate of ^{39}Ar needs to be improved by a factor of 10 – 100 before routine, practical analyses with ATTA can be realized.

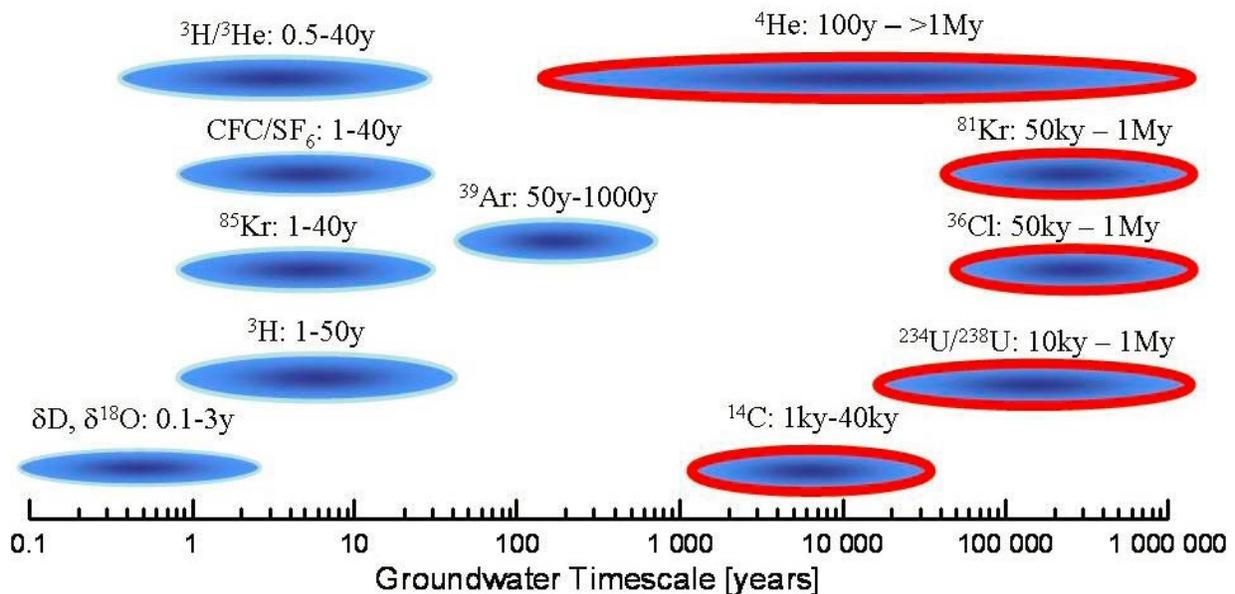


FIG. 1. Dating ranges of ^{85}Kr , ^{39}Ar , ^{81}Kr and other established environmental tracers. Figure reproduced from *Dating Old Groundwater: A Guidebook*, IAEA, Vienna (2012).

3. Atom Trap Trace Analysis

Atom Trap Trace Analysis (ATTA) is a laser-based atom counting method (Chen *et al.*, 1999). At its center is a magneto-optical trap to capture atoms of the desired isotope using laser beams (Fig. 2). A sensitive photo-detector detects the laser induced fluorescence emitted by the atoms held in vacuum. Trapping force and fluorescence detection require the atom to repeatedly scatter photons at a high rate ($\sim 10^7 \text{ s}^{-1}$), a process that is the key to the superior selectivity of ATTA because it only occurs when the laser frequency precisely matches the resonance frequency of a particular atomic transition. Even the small changes in the atomic transition frequency between isotopes of the same element, the so called isotope shifts caused by changes in nuclear size and mass, are sufficient to perfectly distinguish between the isotopes. ATTA is unique among trace analysis techniques in that it is free of interferences from any other isotopes, isobars, atomic or molecular species.

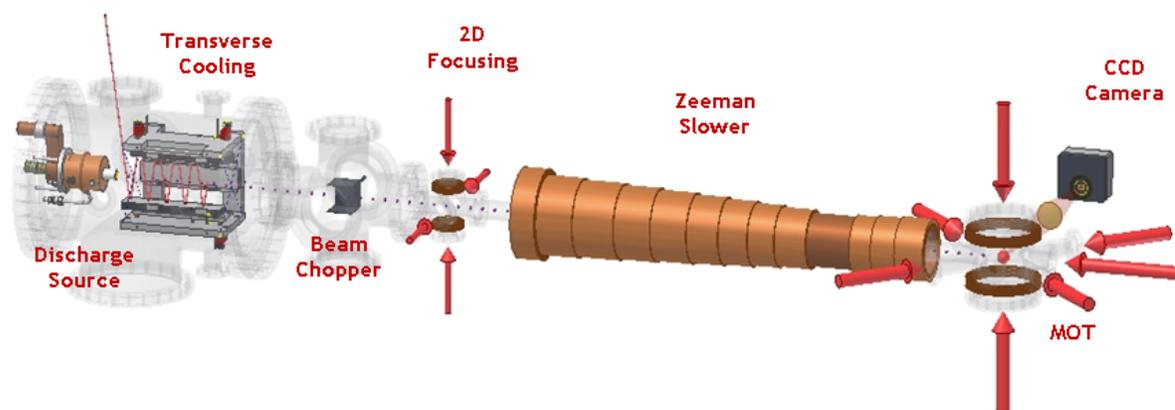


FIG. 2. Schematic of the ATTA-3 apparatus. The total length of the atomic beamline is approximately 2 m. Lasers and optics are located on an adjacent laser table of a similar length.

Following the first demonstration of ATTA (Chen *et al.*, 1999), both the reliability and counting efficiency of the instruments have been steadily improved. With the completion of the ATTA-3 instrument at Argonne (Jiang *et al.*, 2012), for the first time ^{81}Kr -dating became available to the geoscience community at large. In the six month period following November 2011, the Argonne group has measured the $^{81}\text{Kr}/\text{Kr}$ and $^{85}\text{Kr}/\text{Kr}$ ratios in ~ 40 samples that had been extracted by collaborators from groundwater wells in the Great Artesian Basin, Guarani Aquifer (Brazil), and Locust Grove (Maryland); from brine wells of the Waste Isolation Pilot Plant (New Mexico); and from geothermal steam vents in Yellowstone National Park (Yokochi *et al.* 2012). Sample collection and purification were conducted by either the University of Illinois at Chicago or the University of Bern.

The required sample size for applications in ^{81}Kr -dating depends on both the sample age and the desired uncertainty in age determination (Fig. 3). ^{81}Kr -dating with ATTA-3 covers an effective age range from 150 kyr to 1.5 Myr, or 0.6 – 6 times the half-life of the isotope. On the side younger than 150 kyr, the change of $^{81}\text{Kr}/\text{Kr}$ is too small to provide precise age resolution. On the side older than 1.5 Myr, the $^{81}\text{Kr}/\text{Kr}$ ratio itself is comparable to the error introduced by the correction for the memory effect. Within the effective age range, a typical sample size is 5 –

10 micro-L STP of krypton, which can be extracted from approximately 100 – 200 L of water or 40 – 80 kg of ice. For an $^{85}\text{Kr}/\text{Kr}$ analysis, the required sample size is generally smaller by an order of magnitude because of the isotope's higher initial abundance in the atmosphere. It should be noted that these are not absolute requirements. Instead, they should be viewed as a guideline. If needed, extraordinary steps, for example prolonged xenon flushing in order to reduce the memory effect, can be taken to further reduce the required sample size and meet the special demands of a particular application. The chemical purity of the krypton sample is not critical since the ATTA method is immune to contamination from any other species.

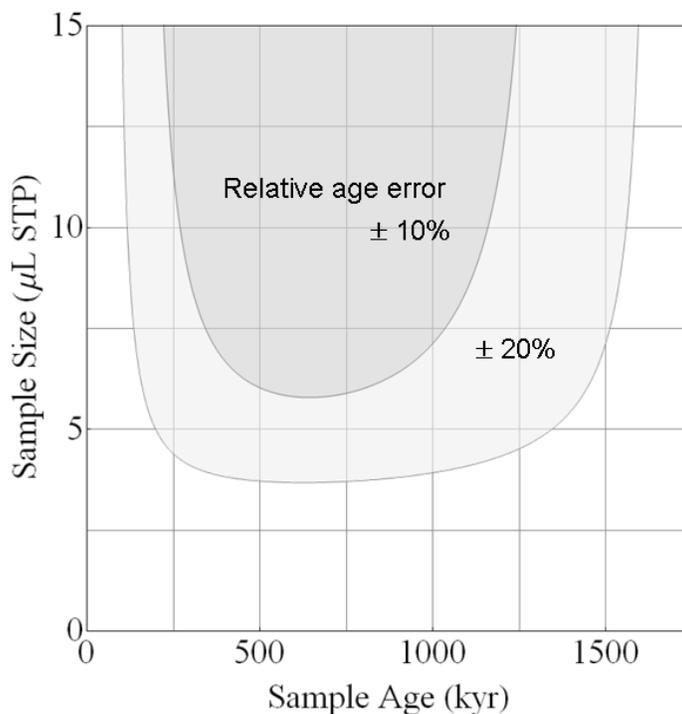


FIG. 3. Sample size vs. sample age and desired accuracy for ^{81}Kr -dating. The two curves are for a relative age error of $\pm 10\%$ and $\pm 20\%$, respectively.

Cross-sample contamination remains the primary limitation on the sample size requirement and sample processing time of ATTA-3. The discharge used to excite krypton atoms causes ionization and the implantation of ions into the surrounding walls. Those embedded atoms of the current and previous samples can later be gradually released back into the vacuum system, causing an instrumental memory effect. This effect is mitigated by flushing the system for 36 hours with a xenon gas discharge following each measurement. This solution significantly limits the sample processing speed as each measurement-flushing cycle takes two days of time even though the measurement itself only takes 2-3 hours. Taking into account the need to calibrate the system regularly with a standard sample, the Argonne group can presently analyze $^{81}\text{Kr}/\text{Kr}$ and $^{85}\text{Kr}/\text{Kr}$ in 120 samples annually. Additional atom traps sharing a common laser system can be introduced to increase the sample throughput at the rate of 120 samples per year per trap.

With future R&D, the flushing time of 36 hours could be shortened. Moreover, the discharge source of metastable atoms may be replaced with a photon excitation scheme (Ding *et al.*, 2007), thus avoiding the undesirable effects due to ionization in the discharge. If successful, the photon excitation scheme will lead to even smaller required sample size and a higher sample processing speed. With photon excitation, the trapping and counting efficiency will be further improved, and the 36-hour flushing will no longer be necessary.

A demonstration experiment was conducted at Argonne in 2010 to show that ATTA-3 can analyze $^{39}\text{Ar}/\text{Ar}$ ratios in both an atmospheric sample at the level of 8×10^{-16} and an old water sample at the level of 1×10^{-16} (Jiang *et al.*, 2011). Indeed no interference from other atomic or molecular species was observed at the 1×10^{-16} level. Counting statistics was the only limitation. The counting rate for the atmospheric sample was only 6 counts per day. In order to perform ^{39}Ar analysis for practical environmental applications, the counting rate needs to be increased by a factor of 10-100. However, no additional R&D has been attempted at Argonne since the proof-of-principle experiment because the instrument has been fully occupied by the aforementioned activity on ^{81}Kr -dating. It should be noted that the size of argon gas samples extracted for ocean ventilation studies, at a few mL-STP, appears adequate for an ATTA analysis.

In addition to the effort at Argonne National Laboratory, a number of groups in other institutions have also engaged in ATTA development, all were present at the workshop:

University of Science and Technology of China (USTC) – The USTC group has collaborated with the Argonne group to develop both the ATTA-3 instrument at Argonne and an ATTA instrument at USTC. Using the ATTA instrument at USTC (Cheng *et al.*, 2010), the group demonstrated the ability to measure $^{85}\text{Kr}/\text{Kr}$ ratios with a precision better than 5% in test samples each containing 8 micro-L STP of krypton. $^{81}\text{Kr}/\text{Kr}$ can also be measured, but the counting rate needs to be improved by an order of magnitude.

Heidelberg University – The Heidelberg group is focused on developing an ATTA system for $^{39}\text{Ar}/\text{Ar}$ analysis (Welte *et al.*, 2010). The group demonstrated a ^{39}Ar count-rate of 15 atoms per day for atmospheric samples. This is more than two times higher than what the Argonne group had demonstrated.

Columbia University – The group in the Physics Department of Columbia University is developing an ATTA system for the purpose of measuring Kr/Xe ratios down to the 10^{-12} level, not in environmental samples, but in highly purified xenon gas samples. Such high purity is required for the next-generation liquid xenon detector of dark matter.

Hamburg University – The group at Hamburg University is developing an ATTA system to monitor atmospheric ^{85}Kr released by nuclear fuel reprocessing plants. If employed by the International Atomic Energy Agency (IAEA), such a system could detect non-compliance to the Non-Proliferation-Treaty (Winger *et al.*, 2005). While the trap is under construction, the group has developed a VUV-lamp that can excite krypton into the metastable state, and operated the lamp for over 500 hours (Daerr *et al.*, 2011).

4. Sampling

4.1. Sample Collection

Specialized methods for sampling and noble gas separation have been developed to satisfy the requirements of the relatively large volumes of Ar and Kr needed for noble gas radionuclide measurements of gas, water, and ice. Earlier, published studies of ^{81}Kr have used gases obtained from ~17 tons (Lehmann *et al.*, 2003) to ~3 tons (Sturchio *et al.*, 2004) of water. Current methods for analysis of ^{39}Ar and ^{81}Kr still require gas extraction in the field. Such gas extraction systems must have the following characteristics: (i) be leak tight to avoid sample contamination by modern air, (ii) have a high extraction yield (> 80%) to minimize the necessary volume of water and extraction time, and (iii) be sufficiently robust for field work, i.e. simple, light and portable. Efficiency optimization also depends on whether the extraction is carried out on land or on a research ship (Smethie and Mathieu, 1986).

Gases can be extracted by exposing the air-saturated water to a gas phase having lower partial pressures of Ar and Kr, which can be achieved either by applying a partial vacuum or by putting the water in contact with a pure and inert gas such as He or N_2 in which Ar and Kr partial pressures are nominally zero. The efficiency of gas extraction from groundwater therefore depends on (i) partial pressures of Ar and Kr in the gas phase, (ii) solubility of Ar and Kr in the water, and (iii) rate of gas transfer. The pressure in the gas phase depends on the capability of the pump and the gas flux, which is a function of the water flux and the gas content of the water. The limiting factor of the gas transfer rate from water to gas phase is the rate of gas diffusion in water. The most effective method of enhancing the efficiency of the apparatus is to increase the specific gas-water interfacial surface area, either by spraying the water or by using a membrane contactor characterized by a large surface area.

During these gas extraction processes, the elemental and isotopic ratios of noble gases are expected to fractionate depending on their solubility. A theoretical limit on the maximum possible isotopic fractionation is given by assuming Rayleigh fractionation using the square root of the mass ratio as the isotopic fractionation factor. For an extraction efficiency of >50%, the isotopic fractionation of the $^{81}\text{Kr}/^{84}\text{Kr}$ ratio is expected to be <1%, much smaller than the uncertainty of the current measurements.

Two categories of systems have been applied in the field for large-volume gas extraction (Fig. 4): (i) vacuum extraction chamber and (ii) membrane contactors. In both systems, sample water is transferred from the well into the system and discharged after gas extraction. Large particles in the water are filtered out, and water flux and inlet pressure are monitored using a flow meter and a pressure gauge. Check valves are used to prevent water or gas from flowing in undesired directions.

In a vacuum extraction chamber, water is sprayed through nozzles of optimal size (2-6 mm) into a transparent cylinder containing two phases, gas and water, separated by gravity. Water is continuously removed from the bottom of the cylinder at a desired rate regulated with magnetic floating sensors to maintain a range of water levels, while gas is transferred to a sample container through a compressor. For air-saturated water with a flux of 20 L min^{-1} , a typical extraction pressure of 20-50 mb is reached. This leads to an extraction efficiency of 80-90% for water at 10°C (Kropf,

1996). The flow rate and thus the sampling capacity of the system is primarily limited by the pump rate of the drainage pump, which is about 30 L min^{-1} . Vacuum extraction systems developed at the Physics Institute, University of Bern, have been used successfully in field campaigns for large volume ^{39}Ar , ^{85}Kr , and ^{81}Kr sampling (Corcho *et al.*, 2007; Lehmann *et al.*, 2003; Sturchio *et al.*, 2004). Similar systems have also been built at other universities or companies (University of Heidelberg, University of Freiburg, University of Leipzig, Hydroisotop GmbH) for research in hydrology and oceanography (Smethie and Mathieu, 1986).

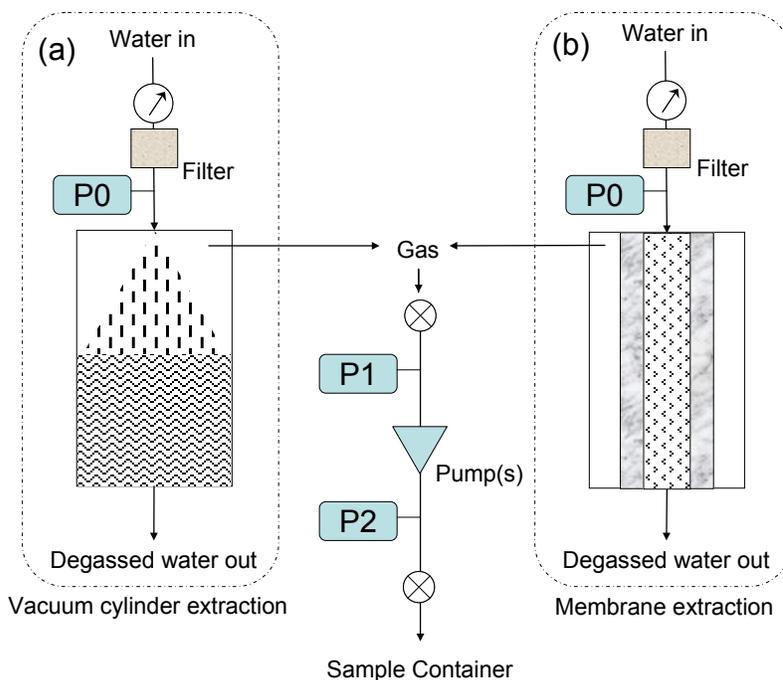


FIG. 4. Schematic diagram of water degassing systems: a) vacuum cylinder extraction; b) membrane extraction. (P0: water inlet pressure; P1: gas extraction pressure; P2: gas pressure in the sample container).

In a hydrophobic microporous hollow-fibre membrane contactor, there are two cylindrical volume sections partitioned by the membrane. Being hydrophobic, the membrane does not allow water to pass through the pores, and diffusion of gas from the liquid water into the gas-filled pores is the mechanism by which gases are extracted from water (Wiesler, 1996). The gas phase in contact with water is maintained at a pressure of 20-150 mb (P1, Fig. 4), and the gas released from the water is pumped into sample containers (P2). The commercially available membranes facilitated the construction of compact field degassing systems (Probst *et al.*, 2007; Ohta *et al.*, 2009). The membrane contactor currently used at the University of Illinois at Chicago (Liqui-Cel® Extra-Flow 4 x 28) handles water flow rates up to 30 L min^{-1} and water temperatures to 70°C . For air-saturated water with a water flux of 20 L min^{-1} at a typical vacuum pressure of 130 mb, the extraction efficiency is 80-90% for Ar and O_2 and $>70\%$ for Kr. No significant Kr isotopic fractionation has been observed through this extraction process. The operating pressure of the vacuum is limited to $>65 \text{ mb}$ to avoid damaging the membrane structure, which sets a theoretical limit on the extraction efficiency. The original system (named EDGAR: Extraction of Dissolved Gases for Analysis of Radiokrypton) weighed about 180 kg (Probst *et al.*, 2007), whereas a recent modification (EDGAR-2) halved the size and has been replicated and modified by groups in Vienna (IAEA), Brazil, and

Heidelberg. Smaller membrane contactors are now available with lower water flow capacity ($< 5 \text{ L min}^{-1}$), and may be applied for sampling smaller volumes (Ohta *et al.*, 2009; Matsumoto *et al.*, 2012).

4.2. Sample Preparation

The measurement of ^{81}Kr by ATTA requires relatively large quantities (5-10 μL) of pure Kr gas, and even larger quantities of Ar are required for low-level counting of ^{39}Ar ($\sim 250 \text{ mL}$ of Ar). The gas phase extracted in the field, with a highly variable composition, has to be processed and purified in the laboratory to produce suitably pure Ar and Kr for analyses. There are several methods to separate noble gases from gas mixtures. Some of the most common processes used in large-volume Kr-Ar purification system are distillation, adsorption, and absorption.

New gas purification techniques and materials (e.g., membranes, nano-tubes, cation-exchanged zeolites) have been developed recently. As the efficiency of ATTA measurements increases and required sample size decreases, separation and purification techniques will converge toward techniques that are presently in use for stable noble gas isotopic analyses (Beyerle *et al.*, 2000). The procedures described here or elsewhere in the literature (Loosli and Purtschert, 2005; Smethie and Mathieu, 1986; Yokochi *et al.*, 2008) are therefore to be regarded as a snapshot of the present capability. Two large-volume noble gas purification systems are presented below.

4.2.1. University of Bern: Ar and Kr

The Physics Institute of the University of Bern has a long history in the separation and analysis of noble gas radionuclides by low-level counting (LLC). In a gas separation setup that was used for most of the published ^{39}Ar studies (Loosli *et al.*, 1983; Loosli *et al.*, 1986; Loosli, 1999; Loosli and Purtschert, 2005), the crude gas was transferred from the sample cylinder into a first cooling trap filled with activated charcoal. Using the permanent gas as a carrier, water vapour and CO_2 were removed by molecular sieve 5A, and O_2 was removed by oxidation of Cu in a furnace at $600 \text{ }^\circ\text{C}$. The sample was then released into a buffer volume, and injected as a sequence of 2-litre aliquots into a gas chromatographic separation system.

Recently a new and more efficient Ar purification system was developed (Reidmann, 2011) (Fig. 5). In the new system Ar is separated in a one-step desorption process from a lithium-cation exchanged faujasite zeolite. Helium is used as the carrier gas. The separation performance for different gas compositions is highly temperature dependent. For example, for Ar-oxygen separation a temperature of $-153 \text{ }^\circ\text{C}$ is optimal. The process temperature is regulated in a vessel (Fig. 5) by liquid-nitrogen cooling and by counter heating of the nine individual stainless-steel columns. The released gas composition is monitored by a quadrupole mass spectrometer. The desorbed argon fraction is finally purified in a getter module. Compared to the process time using the previous setup (2-3 days), argon from 100 litres of air can now be separated within 3-4 hours including the regeneration of the columns.

Kr from typically 300-500 liters of water, or from the aforementioned Ar-Kr separation system is further separated by three GC steps. On the other hand, if only Kr (for ^{85}Kr or ^{81}Kr measurements) is of interest, the procedure starts here (Collon *et al.*, 2000). The sample gas is

exposed to a molecular sieve 5A bed to remove water vapor and CO₂, and subsequently is adsorbed on an AC cold finger. The trap is then heated to room temperature, and the desorbed gases (mainly N₂ and Ar) are pumped away during the first 5 minutes. The trap is then flushed with He carrier gas and the effluent is monitored with a TC detector. After the Ar, O₂ and N₂ peaks have passed, the two-way valve is switched to divert the gas flow through the second trap filled with 5A molecular sieve cooled at LN₂ temperature. From this trap, the desorption procedure is repeated to further purify and freeze Kr in the third cooling trap filled with AC. In each step the gas volume is reduced by a factor of ~10 (Collon *et al.*, 2000). The third cooling trap is then removed from the system and connected to a commercial GC system (Varian Star 3400) where Kr is further purified. If the Kr and CH₄ abundances in the sample are comparable, they can be easily separated and the final amount of recovered Kr is determined from the area of the Kr peak. On the other hand, if the methane and Kr peaks cannot be separated, the Kr content in the counter gas has to be measured by mass spectrometry. Large CH₄ concentration in the sample gas requires further measures in order to purify Kr. For example, CH₄ is oxidized in a CuO-coated furnace at 800°C, followed by the separation of the produced CO₂ and H₂O.

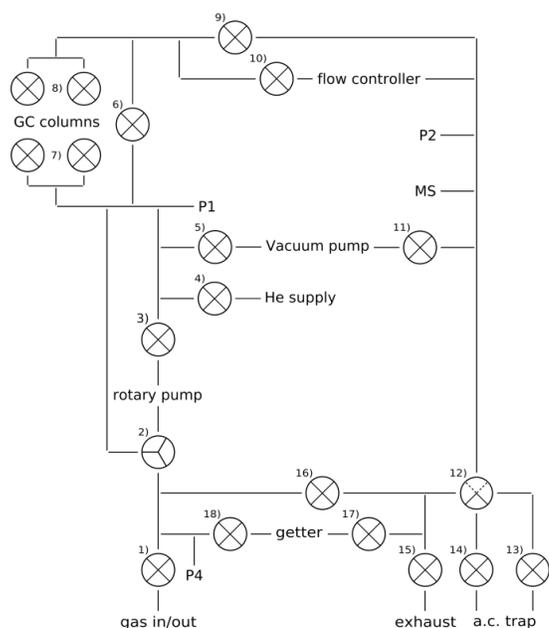


FIG. 5. Ar purification system at University of Bern. The crude gas sample is adsorbed on large GC columns (metal coils on the right picture) and Ar is separated in a single-step desorption process by flushing with a He carrier at 153 K. A getter is used for the final purification.

4.2.2. University of Illinois at Chicago: Kr

Major constituents of atmosphere, N₂, O₂ and Ar, have much higher vapor pressure than Kr. Consequently, cryogenic distillation enriches the residual phase in Kr. Large-scale cryogenic distillation with refined engineering control has indeed been the most widely applied method of producing pure gas substances from the atmosphere. A simple method of cryogenic Kr enrichment at an easily attainable constant temperature (77 K) was developed at the University of Illinois at

Chicago (Yokochi *et al.*, 2008) (Fig. 6). Pure Kr is obtained by subsequent GC separation and Ti-gettering. The system uses a quadrupole mass spectrometer (QMS) to monitor gas effluent composition during separation, which enables (i) small-scale cryogenic distillation in a controlled manner, (ii) gas chromatographic separation of ppm-level Kr from a significantly large quantity of gas (up to a few liters), and brings (iii) the applicability of the method to natural groundwater samples characterized by variable chemical compositions.

After H₂O and CO₂ removal using molecular sieve 4A, sample gas is condensed in an empty container at LN₂ temperature, then distilled at that temperature assisted by a vacuum compressor. The rate of the cryogenic distillation is about 3 L/min for a system dominated by N₂, and 0.5 L/min for a system dominated by O₂. The N₂/Ar ratio of the distillation gas effluent is continuously monitored to determine the progress of the distillation based on a model calculation assuming gas-liquid equilibrium partitioning. Efficient separation of Kr and CH₄ from Ar, O₂, and N₂ can be achieved for up to a few liters of the distillation residue gas by using an activated charcoal column (AC2) at room temperature. The Kr peak following these major species overlaps with the peak tails, but the use of a QMS for monitoring gas composition enables identification and further selective processing of the Kr-enriched portion. Molecular sieve 5A separates Kr from CH₄ (up to a few hundred cm³ STP) at low temperature (around -20°C). Pure Kr is collected in a small (0.7 cm³) stainless steel container filled with activated charcoal.

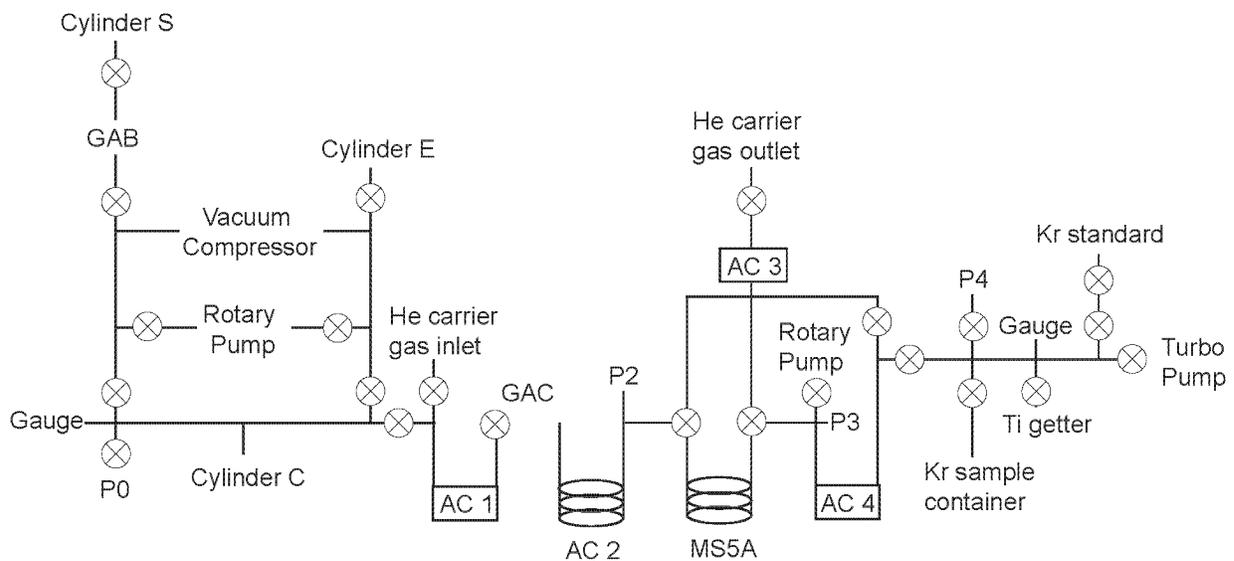


FIG 6. Schematic of the purification system at the University of Illinois at Chicago. Crossed circles represents valves. Circles with filled triangles are three-way valves. Acronyms AC, MS, and P represents activated charcoal, molecular sieve, and port, respectively.

5. Applications in Geosciences

5.1. Groundwater Residence Time

Over 1.5 billion people depend on groundwater as their primary source of drinking water (Clarke *et al.*, 1996). Increases in world population have led to greater demands on groundwater

resources to provide sufficient water for agricultural, industrial, and domestic purposes. Increasing groundwater withdrawals may lead to a higher risk of groundwater pollution from infiltration of inadequately treated wastewaters, as well as reduced groundwater discharge that may affect the amount and quality of surface water flows. Global climate change brings the additional threat of diminished groundwater recharge in large regions. For these reasons it is important to develop a more comprehensive and predictive understanding of the recharge rates, flow paths, and residence times of water in major aquifer systems, to ensure accurate water resource assessments and effective strategies for sustainable withdrawal and protection of water quality. Knowledge of recharge rates gives limits on sustainable yields and artificial recharge; knowledge of flow paths can help resolve transnational boundary disputes relating to groundwater production; and knowledge of water residence time distributions, in conjunction with stable isotope compositions, comprise an archive of climatic information that can give insight into long-term aquifer behavior under conditions of changing climate.

Groundwater age is usually defined as the mean subsurface residence time following isolation from the atmosphere, and it can be estimated either from Darcy's Law (based upon hydraulic conductivity and gradient) or from measurements of time-dependent abundances of environmental tracers. It is one of the most elusive geologic parameters to quantify, despite its crucial significance for water resources, waste management, subsurface reactive transport, and paleoclimate. Groundwater residence times span an enormous range from days to millions of years. However, using numerical simulations to calculate the flow paths and flow rates of groundwater is difficult because of the extreme physical heterogeneity of aquifers. For example, the permeability of earth materials spans approximately 16 orders of magnitude, and the spatial distribution of permeability in aquifers is difficult to characterize. The realistic assessment of water resources and contaminant transport without a valid understanding of flow paths and flow rates is problematic. Environmental tracers that are sensitive to residence times have proven to be effective aquifer evaluation tools because each sample collected from a well contains information regarding the entire upstream velocity field. Environmental tracers are inherently integrative when compared to aquifer physical property measurements such as water level, permeability, conductivity, and local geologic structure.

A variety of chemical and isotopic residence-time tracers have been used widely for characterizing groundwater systems (Fig. 1). Most of these, including tritium, $^3\text{H}/^3\text{He}$, chlorofluorocarbons, and SF_6 , are applicable only to young water, i.e., that recharged within the past ~50 years (Plummer *et al.*, 1993; Cook and Solomon, 1997). Radiocarbon (^{14}C) is useful in the range of ~1,000 to 40,000 years, but complications by dissolution of ancient carbonate minerals and biogenic CO_2 impart high model-dependence to residence times derived from ^{14}C measurements (Plummer and Sprinkle, 2001). None of these tracers effectively address time scales in the critical range of ~100 to ~1,000 years, and few tracers are applicable on a time scale of 10^4 - 10^6 years or more (^{36}Cl and ^4He). The ^{36}Cl method is complicated by variations of the initial ^{36}Cl activity and by subsurface input of both stable chloride and nucleogenic ^{36}Cl (Phillips, 2000; Park *et al.*, 2002). Many groundwater aquifers do not meet the restrictive criteria for application of ^{36}Cl -dating, e.g. those containing saline waters and brines, and therefore the ^{36}Cl tracer cannot be applied for dating such aquifers, although it remains useful for tracing the origin of salinity in such systems (Phillips, 2000). Accumulation of ^4He in aquifer water can thus be used to model groundwater residence time, provided accurate assumptions are made about the rate of supply of ^4He to the pore water from the solid phase, as well as the rate of gain and/or loss of ^4He by advection and diffusion from or to surrounding formations or the atmosphere (Bethke

et al., 1999; Stute *et al.*, 1992). The concentration of ^4He in large, old aquifers commonly reflects input from external sources (Torgersen and Clarke, 1985).

^{85}Kr – The ability to determine residence times of young, shallow groundwaters is particularly important because of the fact that many shallow aquifers have been subject to contamination by hazardous and toxic substances such as solvents, heavy metals, pesticides, herbicides, endocrine disruptors, and radionuclides. Accurate residence time information for shallow groundwaters allows better understanding of the rates of natural attenuation of contaminants, as well as being useful for determining liability and implementing appropriate remediation strategies. The most successful methods available for determining residence times of young (<50 yr) groundwaters are: tritium- ^3He (Schlosser *et al.*, 1988), CFC (chlorofluorocarbon), SF_6 (Plummer and Busenberg, 2000), and ^{85}Kr (Smethie *et al.*, 1992). These methods have been compared in detailed studies at a site on the Delmarva Peninsula in eastern Maryland (Ekwurzel *et al.*, 1994). At this site, residence times estimated from these tracers all agreed within about 2 years, owing to a combination of high recharge rate, insignificant dispersion, negligible mixing with older water, negligible adsorption-desorption or biodegradation processes, and minimal gas loss to the atmosphere.

Although several groundwater dating methods exist in the 0-50 year age range, all methods have limitations and different methods may fail in a given environment for various reasons such as excess air, degassing, biodegradation, and local contamination. In addition, it is recognized that samples from wells, springs, and streams are mixtures of water from multiple sources, flow paths, and travel times, and that apparent ages derived from individual dating methods can be misleading in some cases (Bohlke and Michel, 2009; Eberts *et al.*, 2012; Green *et al.*, 2010). Data from multiple tracers are needed to evaluate problems with individual methods and to resolve age distributions of mixed samples and permit accurate modeling of water movement and chemical transport. ^{85}Kr can be an especially useful tracer for such purposes because it is relatively immune to some of the potential problems and its input history contrasts with those of some other tracers.

The application of the ATTA method to measuring ^{85}Kr in young groundwater has several advantages over existing methods: (1) the decline of CFC input to the atmosphere and the decay of the bomb-produced tritium pulse have begun to reduce the age resolution of these methods; (2) Kr is unaffected by redox reactions such as those involved in biodegradation of CFCs; (3) there is a smaller likelihood of local point sources of ^{85}Kr than is the case for CFCs and SF_6 (e.g. in landfills); and (4) ATTA measures the ratio of $^{85}\text{Kr}/\text{Kr}$, which is relatively insensitive to gas loss, in contrast to the tritium-helium, CFC, or SF_6 methods. In addition, the $^{85}\text{Kr}/\text{Kr}$ ratio is not sensitive to recharge temperature or elevation, or to the presence of excess air.

^{81}Kr – Some major aquifer systems are dominated by water that has no measurable ^{14}C , implying residence times exceeding ~40,000 years. This pertains especially to the deeper, confined portions of these aquifer systems. Examples are found in the Great Artesian Basin of Australia, the Nubian Aquifer of Egypt-Libya-Chad-Sudan, and the Guarani Aquifer of Brazil-Argentina-Paraguay-Uruguay. Without knowledge of residence time distributions, it is difficult to construct and validate numerical hydrodynamic models for developing groundwater management strategies that will ensure the optimal use of these critically important water resources by future generations. ATTA measurements of ^{81}Kr enable unprecedented insights into residence times of old groundwater, providing crucial validation to three-dimensional, basin-

wide hydrodynamic models. The first application of ATTA (using ATTA-2) to groundwater hydrology determined residence times of old groundwater in the Nubian Aquifer located underneath the Sahara Desert in Western Egypt (Fig. 7) (Sturchio *et al.*, 2004). The results of this study revealed the groundwater age and hydrologic behavior of this huge aquifer, with important implications for climate history and water resource management in the region. Also demonstrated was the consistency between ^{81}Kr and ^{36}Cl measurements, and there were near-blank activities of ^{14}C and ^{85}Kr in these waters as expected. Additional studies of old aquifers using ^{81}Kr are now in progress (e.g., the Great Artesian Basin in Australia and the Guarani Aquifer in South America).

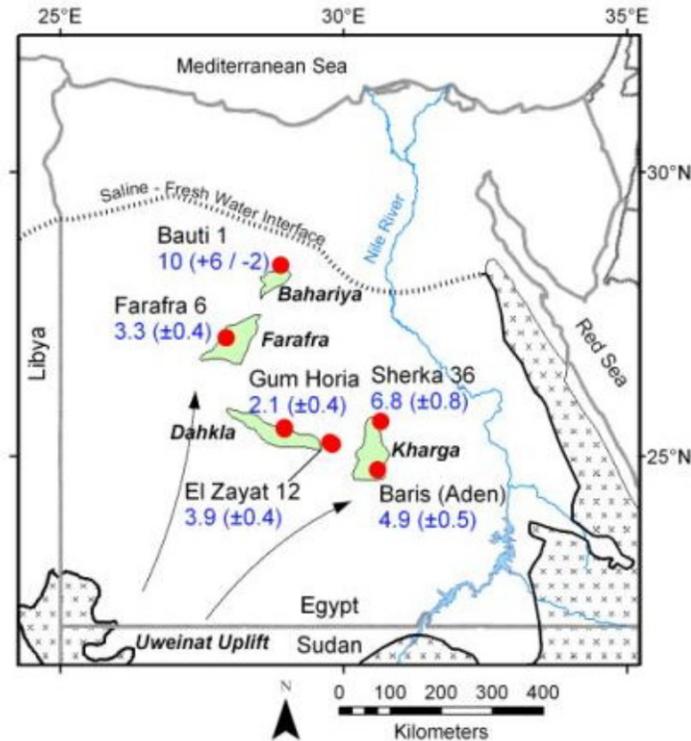


FIG. 7. Map showing sample locations (red circles) and their apparent ^{81}Kr ages (in units of 10^5 years) in relation to oasis areas (shaded green), Precambrian basement outcrops (patterned), and other regional features. Groundwater flow in Nubian Aquifer is toward the northeast from a recharge area near the Oweinat Uplift in SW Egypt (Sturchio *et al.*, 2004).

$^{39}\text{Ar} - ^{39}\text{Ar}$ has been shown to be useful in some cases as a tracer for groundwater residence times in the range of 50-1,000 years (Corcho *et al.*, 2007). In contrast to ^{81}Kr and ^{85}Kr , which have negligible subsurface production, ^{39}Ar has a substantial subsurface source from the nuclear reaction $^{39}\text{K}(n,p)^{39}\text{Ar}$. In some studies of ^{39}Ar in groundwater, an isotopic abundance of ^{39}Ar in excess of the atmospheric abundance has been observed, indicating that nucleogenic ^{39}Ar from the aquifer rock is transferred to the fluid phase (Loosli, 1983; Andrews *et al.*, 1989). This excess ^{39}Ar is usually considered as an obstacle to determining groundwater residence times (Corcho *et al.*, 2007), but may be useful in combination with radiogenic ^{40}Ar as an indicator of groundwater residence times over a much wider range than that limited by simple decay of cosmogenic ^{39}Ar (Yokochi *et al.*, 2012).

Hydrologists at the TANGR 2012 workshop noted the following in terms of both the importance and the implementation of ^{39}Ar and ^{81}Kr in critical groundwater research:

- Sample size is an important issue for groundwater studies, especially in low permeability formations. Ultimately, sample volumes of 1 L or less would be desirable; however, *many* important regional aquifers yield large amounts of water and, provided that efficient systems are employed for gas extraction in the field, the present sample size of about 100-200 L is workable. Implementation of ^{81}Kr and ^{39}Ar to these regional aquifer systems should start immediately, while analytical advances that reduce sample size continue in order to expand the utility of these tracers.
- Data sets for groundwater studies are inherently small due to the high cost of monitoring wells. This makes the use of integrative tracers such as ^{81}Kr and ^{39}Ar even more important. A limited number of shallow aquifer studies at intensively-monitored sites has occurred, but there is a need for such campaigns at larger (10s to 100s of km) scales.
- Many groundwater systems are rapidly changing due to recent pumping. Recharge rates that lead to the current distributions of tracer concentrations may no longer exist. It is critical that integrative tracers such as ^{81}Kr and ^{39}Ar be measured in systems before additional (and sometimes massive) pumping occurs in order to effectively utilize these tracers for evaluating the hydraulic properties of the aquifer. This fact makes the implementation of residence time tracers urgent to accomplish before critical information is lost.
- The utility of existing tracers such as ^{14}C and ^4He could be greatly enhanced by calibrating them against geochemically simple tracers such as ^{81}Kr and ^{39}Ar . Such calibrations could greatly enhance existing data sets along with new data collection efforts.
- The nature of groundwater transit times in samples collected from wells and discharge locations such as seeps and springs is such that a typical sample contains a large range of values. This makes the use of multiple tracers that speak to different transit times important (Corcho *et al.*, 2007). Without tracers such as ^{81}Kr and ^{39}Ar , there can be an inherent bias in the interpretation of multiple tracer data sets.

5.2. Ocean Ventilation

Ventilation is the primary conduit for passing signals from the atmosphere and the climatic system to the interior of the ocean. For instance ventilation directly influences the distributions and controls of natural and anthropogenic carbon (both organic and inorganic), which in turn directly influences the CO_2 concentration in the atmosphere, and hence the radiative forcing of the earth's climate system. The CO_2 invasion into the interior ocean also influences the pH of the ocean and the saturation state of aragonite and calcite, two important minerals for shell building marine organisms. Ventilation of the ocean transports heat from the atmosphere to the interior ocean where the high heat capacity of the ocean, as compared to the atmosphere, is important for the climate. Similarly, ventilation processes are responsible for transporting oxygen to the interior ocean from the surface, where gas exchange with the atmosphere and photosynthesis

drive an oxygen flux to the ocean. The oxygen concentration in the ocean is important for marine life and for several biogeochemical processes, such as de-nitrification, a process that removes bioavailable nitrogen from the ocean in low oxygen environments. Changes in ocean ventilation will thus not only directly impact the global climate but also has consequences for marine biology, and in the end will impact society through factors such as sea-level rise, climate and fishery sustainability.

Ventilation rates of the ocean can be determined by measurements of tracers. For instance, oxygen levels have been used for this purpose, although that involves assuming a value for oxygen consumption rates. More accurate estimates can be made with tracers that are conservative in the ocean. The most commonly used tracers are tritium- ^3He , the chlorofluorocarbons (CFCs) that were introduced since the 1940's to the atmosphere, or SF_6 that has been entering the atmosphere since the early 1960's. For waters with slower ventilation the most commonly used tracer is radiocarbon (^{14}C). The $\Delta^{14}\text{C}$ age has some systematic uncertainty mainly due to the long equilibrium times with the oceanic carbonate system in the surface mixed layer (on the order of 10 years), i.e. newly ventilated surface waters initially have a non-zero age on the “ $\Delta^{14}\text{C}$ -clock” (Matsumoto, 2007). There are also small uncertainties associated with downward flux of organic particles that dissolve in the deep ocean. By accounting for the “reservoir-age” of the surface mixed layer, Matsumoto (2007) estimated the ventilation ages of the deep-ocean to be less than 1000 years in most areas except the North Pacific.

^{39}Ar observations would fill a gap in ocean observations. Large areas of the ocean, particularly the deep Indian and Pacific Oceans, are filled with “old” water that does not contain CFCs or other anthropogenic tracers. Argon equilibrates with the atmosphere rapidly (on the order of days to weeks) so that most of the ocean surface can be considered as saturated with respect to the $^{39}\text{Ar}/\text{Ar}$ ratio, with the exception of the Southern Ocean (Schlosser *et al.*, 1994a) and Arctic Ocean (Schlosser *et al.*, 1994b) where deep water can be formed under the ice. The well-known input function at the surface for most of the ocean, the chemical inertness of argon, and the half-life of 269 years combine to make ^{39}Ar ideal for deep ocean ventilation studies.

A limited number (~125) of interior ocean ^{39}Ar data are available from large volume sampling and decay counting; most (but not all) of the sample locations are shown in Fig. 8. One of the few available depth profiles is shown in Fig. 9, where some of the world's oldest oceanic water was sampled in the 1970's in the northeastern Pacific Ocean. The profile shows increasing age through the water column to a minimum ^{39}Ar concentration at intermediate depths and increasing concentration towards the bottom due to the influence of Antarctic bottom water spreading northward.

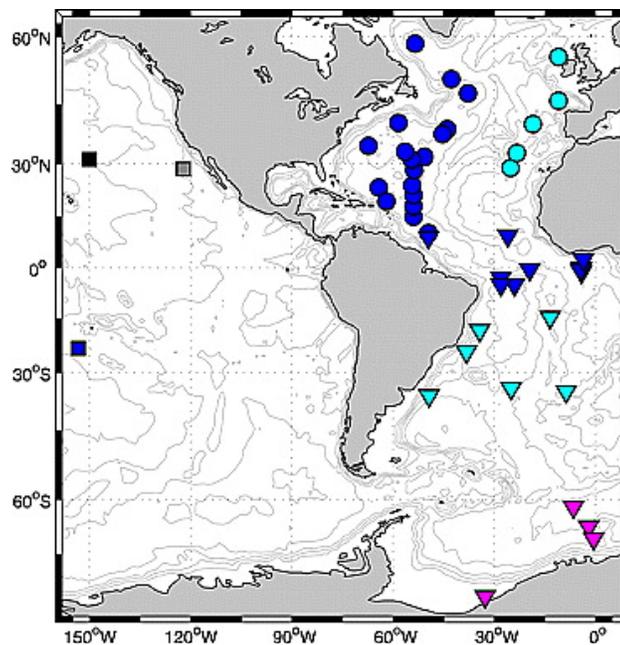


FIG. 8. Locations of interior ocean ^{39}Ar measurements (Holzer and Primeau, 2010).

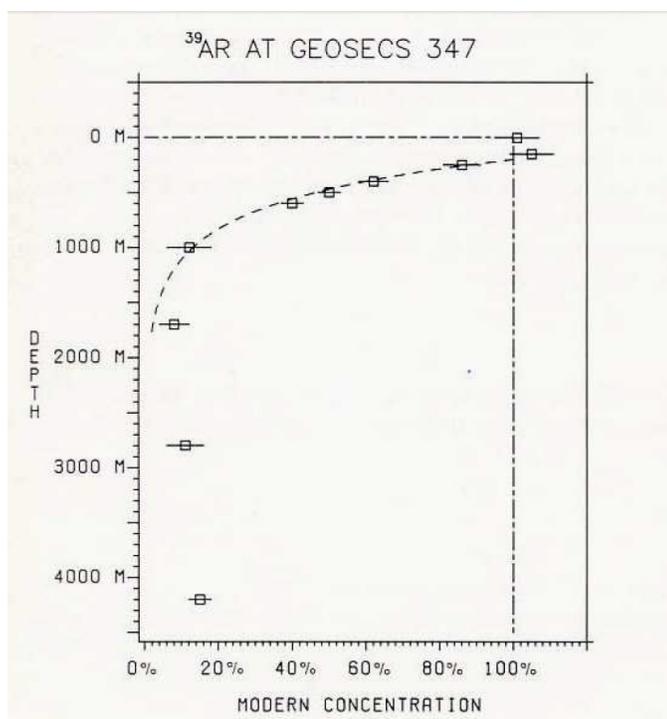


FIG. 9. ^{39}Ar profile from the northeast Pacific Ocean sampled during the GEOSECS expedition (Loosli, 1989).

Holzer and Primeau (2010) used these measurements in a formal study to show that the ^{39}Ar data could reduce the uncertainty in ocean ventilation (represented as a distribution of water parcel transit times from their origins at the ocean surface) by, on average, about 50% as compared to a case where only CFCs and ^{14}C were considered. The reduction in uncertainty is particularly significant for water with long ventilation times, such as in the deep Pacific Ocean where the CFCs have not penetrated, as well as regions with low CFC concentrations such as the deep thermocline where a large amount of older CFC-free water has mixed with a small amount of younger CFC bearing water. They conclude their study by stating that *“It is no question that an effort to produce a globally gridded ^{39}Ar data set would greatly help reduce the uncertainty in our knowledge of oceanic transport and ventilation, which in turn would greatly benefit rigorous estimates of the ocean’s ability to take up and sequester anthropogenic carbon.”*

Similarly, a study by Broecker and Peng (2000), which compared ^{39}Ar and ^{14}C ages of the deep ocean, concluded that *“It is clear that a more dense survey of ^{39}Ar with higher accuracy measurements would prove of great value in constraining ocean general circulation models.”* Taken together, ^{39}Ar and ^{14}C provide strong constraints on the ratio of mixing to advection in the deep ocean.

Opportunities for future measurements of ^{39}Ar include a suite of about 1000 samples from the Atlantic Ocean collected in the 1980s. These samples have been measured for ^{14}C , are available and would constitute an excellent baseline for characterizing Atlantic deep ocean ventilation about 30 years ago. The geographic coverage of these samples is remarkably good (Fig. 10). For future sampling there are ample opportunities to collect samples on, for instance, GO-SHIP repeat hydrography (<http://www.go-ship.org>) that repeats oceanographic sections on a 10 – 15 year time scale to document changes in ocean properties, and / or during cruises within the GOETRACES project (<http://www.geotraces.org/>) that will be mapping the global ocean distributions of various trace elements and isotopes over the next decade.

The Pacific Ocean (3 stations) and the Indian Ocean (no samples) are heavily under-sampled with respect to ^{39}Ar . These two ocean basins have the oldest deep water, i.e. ^{39}Ar data would be particularly useful for these basins. Conducting repeat ^{39}Ar measurements in the Atlantic Ocean for a comparison of ventilation ages between the early 1980’s and the 2010’s would also be interesting.

Sampling of roughly 1000 samples in the Pacific Ocean, 500 in the Indian Ocean, 200 in the Arctic Ocean and 300 repeat samples in the Atlantic Ocean would provide a reasonable one-time coverage. This would mean ~2000 new samples and measurements of 1000 archived samples. There are two important considerations for future measurements and sampling. The desirable measurement precision should provide an age resolution of about ± 25 years, comparable to the age resolution of ^{14}C measurements, which ranges from ± 15 to ± 30 years. Ideally the sample should require a volume of 1 L, or less, of sea-water so that the samples can be drawn in parallel to other samples. Sample sizes of up to about 8 L would also be feasible using the standard 10-L sample bottles for collection.

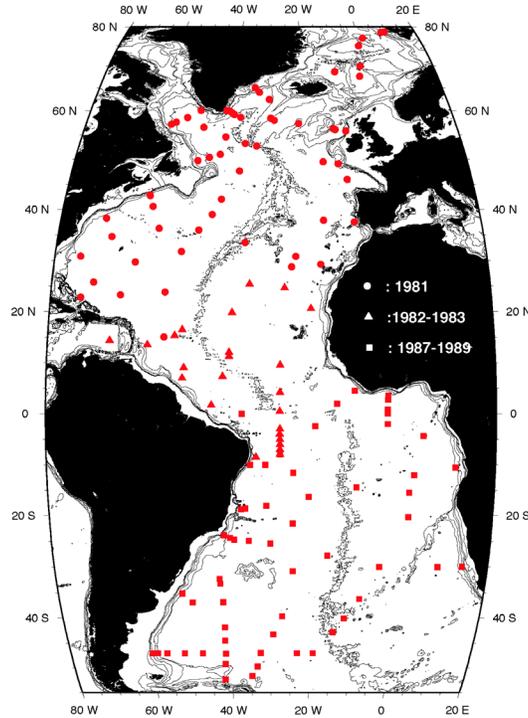


FIG. 10. Locations of oceanographic stations where large volume (250 liters) samples were collected for measurement of ^{14}C and ^{85}Kr . Either the argon fractions or the entire extracted gas samples have been archived at Lamont-Doherty Earth Observatory.

5.3. Ancient Glacial Ice

Polar ice cores have been used to reconstruct Earth's past climate and atmospheric composition as far back as 800,000 years (Jouzel *et al.*, 2007). A range of techniques is used for the dating of ice cores, including annual layer counting, ice flow modeling, age marker synchronization and orbital tuning. Radiometric dating tools for old ice are currently not widely used because of several distinct drawbacks. Radiocarbon dating on the CO_2 present in air bubbles is complicated by *in situ* cosmogenic ^{14}C production in the ice (Lal *et al.*, 1990). Other radiometric methods with limited precision rely on the incidental inclusion of meteorites, tephra layers or organic impurities (Dunbar *et al.*, 2008; Jenk *et al.*, 2007).

^{81}Kr could potentially be used for dating of old ice with ages ranging from 100 kyr - 1500 kyr (Oeschger, 1987). ^{81}Kr dating has several advantages: (1) the technique is widely applicable as all polar ice contains air bubbles; (2) the technique does not require a continuous or undisturbed ice stratigraphy; (3) there is no *in situ* ^{81}Kr production, as is the case for ^{14}C ; (4) the dating method gives an absolute age estimate. The main disadvantage is the large sample size (>40 kg), which has so far precluded its use in ice core studies.

Old ice can be obtained not only from deep ice cores, but also at ice margins and Antarctic blue ice areas (BIAs) where it is being re-exposed by ablation (Sinisalo and Moore, 2010). For paleoclimate studies this provides an interesting alternative to ice coring, as large volume samples can easily be obtained. During the last few years the ice ablating at the Taylor Glacier

BIA (Fig. 11) has been dated using stratigraphic matching techniques (Petrenko *et al.*, 2006). An experiment is being carried out to use the well-dated stratigraphy of Taylor Glacier to test the feasibility and accuracy of ^{81}Kr -dating of old ice for the first time (Buizert *et al.*, 2012). If successful, the experiment would demonstrate that ^{81}Kr -dating is indeed feasible. This could pave the way for reliable ^{81}Kr -dating of other BIAs, which would significantly enhance the scientific value of BIAs in Antarctica. As the required sample size continues to decrease, ^{81}Kr dating of ice core samples might be possible in the future.

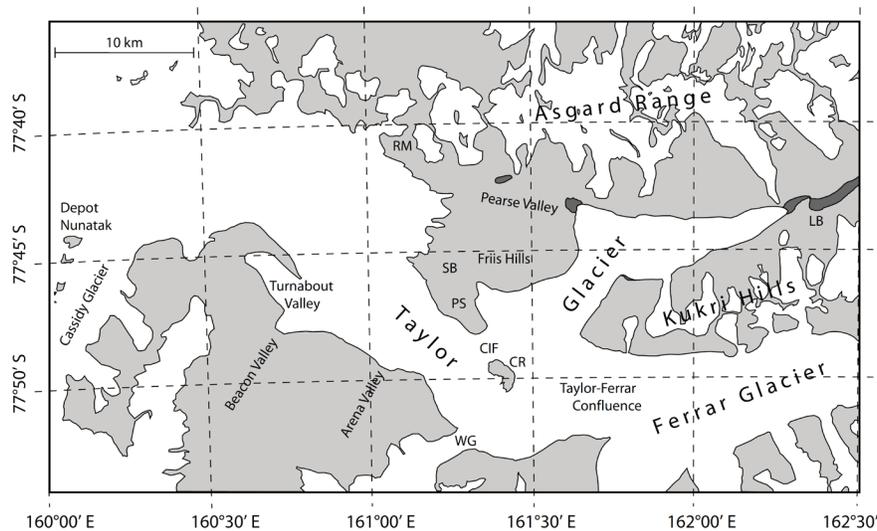


FIG. 11. Taylor Glacier is an outlet glacier of the East Antarctic ice sheet that originates at Taylor Dome, and terminates in Taylor valley of the McMurdo Dry Valleys, Victoria Land. The map shows the lower reaches of the glacier where sublimation-driven ablation exceeds snow accumulation, giving rise to a blue ice area (BIA).

5.4. Fluid Residence and Migration in the Crust

The Earth's crust is a vast reservoir of resources formed via natural geological processes driven by crustal fluids and fluid flow (Fig. 12). Crustal fluids mediate chemical reactions, and transport, concentrate or disperse elements in the crust. They also play the role of messengers by transporting volatiles from the deep Earth through fluid advection. In this context, determining the origin of crustal fluids, the time scales of fluid transport and residence are essential for understanding the geochemical cycle of elements, as well as risk and resource management. For instance, although interactions between groundwater and gas, oil and hydrothermal fluids have been well studied, the fluid migration rate or storage time in crustal reservoirs has rarely been determined due to the lack of optimal tracers. The ability to routinely analyze fluid samples for noble gas radionuclides (^{39}Ar , ^{81}Kr and ^{85}Kr) will provide an indispensable tool for deriving a thorough understanding of the origin, evolution and migration of crustal fluids. Two relevant examples are provided below for volcanic and natural hydrothermal systems.

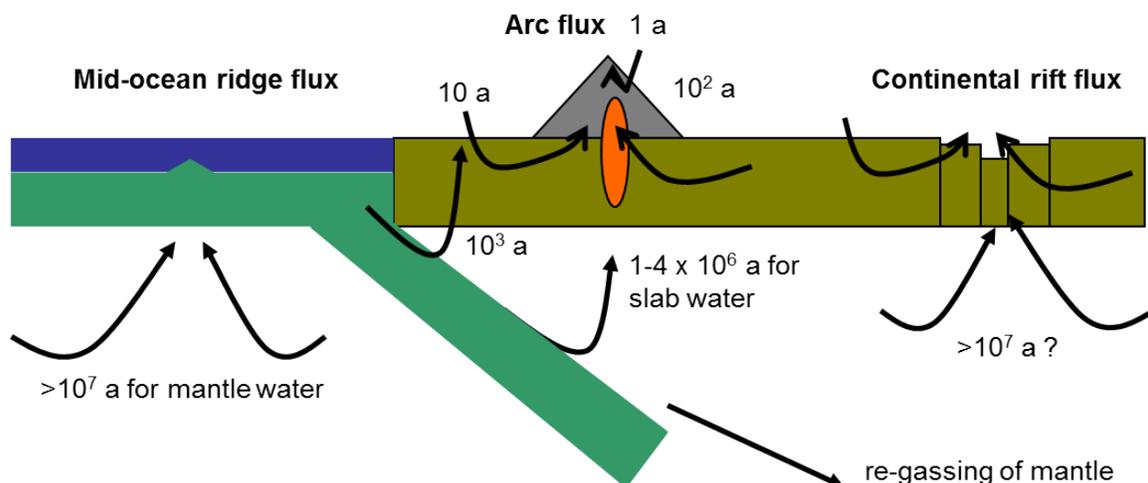


FIG 12. Towards a better understanding of the water cycle and the rates of water exchange between the surface and deep Earth (numbers are estimates of the age of water in various locations)

Constraints on the deep water cycle based on volcanic and hydrothermal gas emissions – Fluids discharging from hydrothermal and volcanic systems through fumaroles, hot springs and geothermal wells are dominated by water (> 90%), CO₂, sulfur (SO₂ and H₂S), and chlorine. In addition to these major components, N₂, H₂, CH₄, CO, HF and the noble gases generally contribute to the gas composition. Work over the past two decades has utilized the technique of combining helium (³He and ⁴He) with other stable isotope systems to estimate the relative contributions of C and N from the mantle, the subducting slab, and atmospheric and crustal sources (see reviews by Hilton *et al.*, 2002; Sano and Fischer, 2012). This work has provided insights into the recycling of volatiles from the Earth's surface to the interior through subduction with implications for the evolution of mantle volatile compositions and the exchange between deep earth and surface reservoirs.

While the sources of C and N in these systems are relatively well constrained in terms of mantle wedge, slab and crust, the ultimate sources of water and sulfur remain somewhat more enigmatic. In addition and perhaps more significantly, the timescales of volatile exchange between the Earth's interior and the atmosphere is currently mainly constrained by models involving stable isotopes (Marty, 1989; Marty and Dauphas, 2003; Marty and Tolstikhin, 1998). In the mantle water is the most significant volatile species due to its abundance and effect on melting and element transport processes (Wallace, 2005). Mantle derived water lowers the melting point of mantle peridotite which ultimately results in water-rich and highly explosive arc magmas (Tatsumi, 1989). On the other hand, surface derived water (i.e. meteoric water) is the driving force for surficial water-magma interactions resulting in highly explosive phreatic eruptions. Meteoric water is also the agent for heat transfer from the magma to the surface in volcanic hydrothermal and geothermal systems. Therefore, understanding the source and relative proportions of magmatic (mantle derived) versus meteoric water is critical for evaluating the global deep water cycle as well as investigating the sources of heat in geothermal systems.

Global data suggest the existence of an end-member in $\delta^{18}\text{O}$ and δD space that is related to water derived from the devolatilization of the subducting slab. In the crust or close to the surface

this “arc-type” water mixes with meteoric water resulting in isotopic compositions that lie along mixing lines extending from the meteoric water end-member to the arc-type water end-member (Giggenbach, 1992; Taran *et al.*, 1989). The endmember composition of arc-type water has been confirmed by δD measurements of H_2O in melt inclusions from volcanic arcs, supporting the idea of a unique slab-derived water end-member (Shaw *et al.*, 2008). The issue with such an end-member, however, is that there is rarely a correlation of δD with the total H_2O content of the gas discharges and that some samples have δD values suggesting almost 100% of the discharging steam to be of magmatic/slabderived origin. Similarly, there is no correlation between the water content of melt inclusions and the δD values. Therefore, one may argue that the arc-type stable isotopic composition is the result of a fractionation process of meteoric water in the crust rather than an end-member phenomenon. If water discharging from high temperature fumaroles is found to be mainly of meteoric rather than mantle or slab origin, it would have profound implications for the global water cycle.

Application of ^{81}Kr , ^{85}Kr , and $^{39}Ar/^{40}Ar$ measured in volcanic emissions that have stable isotope signatures of slab-derived water, combined with other geochemical tracers (C, N, He isotopes and abundance ratios), would provide unprecedented insights into the ultimate source and age of the fluids transporting these gases. For instance slab derived water is expected to have an age on the order of 1 Myr (datable with ^{81}Kr) and surface (meteoric water) that has interacted with the crust would have expected ages of 10^2 - 10^3 years (datable with ^{39}Ar). In contrast, shallow and surface derived water is expected to be relatively young (< 100 years and datable with ^{85}Kr). The combination of radionuclide dates with O and H stable isotopes as well as water fluxes constrained with other methods has the potential of elucidating the extent and rate of water release from the Earth’s interior, transport of water into the deep mantle (re-gassing of the mantle) and evaluating the rates of surface water transport to and from crustal magma reservoirs. Similar investigations at continental rifts could provide complementary insights on the time scales of mantle water degassing (Fig. 12). On a smaller scale, the rate of heat exchange between crustal magma bodies and adjacent geothermal reservoirs could be determined by relationships of heat versus age and source of geothermal water sampled at the surface. This approach could provide valuable insights into the potential longevity of a geothermal system and could be a powerful tool in managing the geothermal resource. This application is further discussed in the next example.

Tracing residence times of crustal fluids by combining atmospheric and crustal derived radionuclides – In addition to the atmospheric derived radionuclides (^{39}Ar , ^{81}Kr and ^{85}Kr), crustal fluids can acquire stable and radioactive noble gases (e.g. 4He , ^{40}Ar and ^{39}Ar) that are continuously produced by the decay of U, Th and ^{40}K , and by nuclear reactions in the crustal minerals. These “crustal” stable and radionuclides may be released from their production sites and incorporated into the fluid as additional natural spikes to trace fluid flow and residence ages. Their concentrations in a crustal fluid will be a function of the accumulated concentrations and production rates in the reservoir rock and the rate of transfer from the rocks to the fluid phase. In the absence of subsurface production and/or transfer of those isotopes into the fluid phase, the fluid migration time between two sites within a flow path can be determined simply by measuring the abundance of a single atmospheric derived radionuclide with an appropriate half-life. The best example of such geochemical tracer is ^{81}Kr , which has no known production path in crustal minerals and can only be derived from the atmosphere. In the case where transfer of subsurface-produced isotopes from the rocks to the fluid phase occurs, the concentration of

radiogenic stable isotopes in the fluid phase will increase with time or flow distance in the same manner as radiogenic ^4He and ^{40}Ar . However, due to uncertainties related to prior accumulation and release rates from crustal minerals, they have not been used routinely as reliable groundwater chronometers. By combining radiogenic ^{40}Ar with nucleogenic ^{39}Ar , which acquires a steady-state concentration in minerals after ~ 1800 years, uncertainties related to poorly constrained release rates can be minimized. Accordingly, the migration time of a fluid between two points within a single flow path can be determined using the ratio of radiogenic $^{40}\text{Ar}^*$ and ^{39}Ar . As with other systems, ^{85}Kr can be used as an unprecedented and unique tracer of atmospheric contamination, distinguishing modern atmospheric contributions from ancient ones.

In crustal fluids, stable noble gases have been used for investigating the processes occurring in subsurface reservoirs, during (i) migration of geothermal fluids (Sano and Wakita, 1985; Kennedy *et al.*, 1987), (ii) evolution of hydrocarbon reservoirs (Ballentine *et al.*, 1991; Hiyagon and Kennedy, 1992; Pinti and Marty, 1995; Kennedy *et al.*, 2002), and (iii) pilot or analogue studies of geological CO_2 sequestration (Gilfillan *et al.*, 2008, Gilfillan *et al.*, 2009). Noble gas radionuclides add enhanced capability of determining the time scales of these processes and fluid migration. Furthermore, the rate of release of radiogenic and nucleogenic noble gases from the production sites in minerals to the fluid phase may also be determined uniquely through the studies of noble gas radionuclides (Yokochi *et al.*, 2012a), which is fundamental to the behavior of volatile elements in geochemistry.

In order to demonstrate proof of concept, a pilot study of noble gas radionuclides in an active geothermal system was performed at Yellowstone National Park (Yokochi *et al.*, 2012b). Prior studies of the Yellowstone system using stable noble gas isotopes show that the thermal fluids contain a mixture of atmospheric, mantle, and crustal components. The ^{39}Ar isotopic abundances in air-corrected samples exceeded those of atmospheric Ar by 525 to 1352%, indicating substantial contributions to the thermal fluids by the reservoir lithologies. With the reasonable assumption that the fluid acquired its crustal component of Ar from the Quaternary volcanic rocks of the Yellowstone caldera, upper limits on deep thermal fluid mean residence times, estimated from $^{39}\text{Ar}/^{40}\text{Ar}^*$ ratios, ranged from 121 to 137 kyr for features in the Gibbon and Norris Geyser Basin areas, and are < 19.6 kyr in Lower Geyser Basin. ^{81}Kr isotopic abundances in the same Gibbon and Norris Basin samples are modern, yielding upper limits on residence time that are consistent with those obtained from $^{39}\text{Ar}/^{40}\text{Ar}^*$ ratios.

References

- Althaus R., Klump S., Omnis A., Purtschert R., Kipfer R., Stauffer F. and Kinzelbach W. (2009) Noble gas tracers for characterisation of flow dynamics and origin of groundwater: A case study in Switzerland. *Journal of Hydrology* **370**, 64-72.
- Andrews J. N. et al. (1989) The in-situ production of radioisotopes in rock matrices with particular reference to the Stripa granite. *Geochimica et Cosmochimica Acta* **53**, 1803-1815.
- Ballentine C., O'niions R., Oxburgh E., Horvath F. and Deak J. (1991). Rare gas constraints on hydrocarbon accumulation, crustal degassing and groundwater flow in the Pannonian Basin. *Earth and Planetary Science Letters*, **105**(1-3), 229-246.
- Bethke C.M., Zhao X. and Torgersen T. (1999) Groundwater flow and the ^4He distribution in the Great Artesian Basin of Australia. *J. Geophysical Research* **104**, 12, 999-13,011.
- Beyerle U., Aeschbach-Hertig W., Imboden D. M., Baur H., Graf T., and Kipfer R. (2000) A mass spectrometric system for the analysis of noble gases and tritium from water samples. *Environ. Sci. Technol.* **34**, 2042-2050.
- Bohlke J.K. and Michel R.L. (2009) Constrasting residence times and fluxes of water and sulphate in two small forested watersheds in Virginia, USA. *Sci. Total Environ.* **407**, 4363-4377.

- Broecker W. S. and Peng T. H. (2000) Comparison of ^{39}Ar and ^{14}C ages for waters in the deep ocean, *Nucl. Instr. Meth. B* **172**, 473-478.
- Buizert C. et al. (2012) Radiometric dating of ancient glacial ice using ^{81}Kr . Abstract for TANGR2012 Workshop.
- Chen C.-Y., Li Y. M., Bailey K., O'Connor T. P., Young L. and Lu Z.-T. (1999) Ultrasensitive isotope trace analysis with a magneto-optical trap. *Science* **286**, 1139-1141.
- Cheng C.-F., Jiang W., Yang G.-M., Sun Y.-R., Pan H., Gao Y., Liu A.-W. and Hu S.-M. (2010) An efficient magneto-optical trap of metastable krypton atoms. *Rev. Sci. Instrum.* **81**, 123106.
- Clarke R., Lawrence A. and Foster S. (1996) *Groundwater: A Threatened Resource*. United Nations Environment Programme Environment Library No. 15, Nairobi, Kenya.
- Collon P. et al. (1997) Measurement of ^{81}Kr in the atmosphere. *Nucl. Instrum. Methods. B* **123**, 122.
- Collon P. et al. (2000) ^{81}Kr in the Great Artesian Basin, Australia; a new method for dating very old groundwater. *Earth Planet. Sci. Lett.* **182**(1), 103-113.
- Collon P., Kutschera W. and Lu Z.-T. (2004) Tracing Noble Gas Radionuclides in the Environment. *Annu. Rev. Nucl. Part. Sci.* **54**, 39-67.
- Cook P. G. and Solomon D. K. (1997) Recent advances in dating young groundwater: chlorofluorocarbons, $^3\text{H}/^3\text{He}$, and ^{85}Kr . *J. Hydrology* **191**, 245-265.
- Corcho J. A., Purtschert R., Barbecot F., Chabault C., Rüedi J., Schneider V., Aeschbach Hertig W., Kipfer R. and Loosli H. H. (2007) Constraining groundwater age distribution using ^{39}Ar : a multiple environmental tracer (^3H , ^3He , ^{85}Kr , ^{39}Ar and ^{14}C) study in the semi-confined Fontainebleau Sands aquifer (France). *Water Resources Research* **43**(W03427).
- Daerr H. et al. (2011) A novel vacuum ultra violet lamp for metastable rare gas experiments. *Rev. Sci. Instrum.* **82**, 073106.
- Ding Y., Hu S.-M., Bailey K., Davis A. M., Dunford R. W., Lu Z.-T., O'Connor T. P. and Young L. (2007) Thermal beam of metastable krypton atoms produced by optical excitation. *Rev. Sci. Instrum.* **78**, 023103.
- Dunbar N. W., McIntosh W. C. and Esser R. P. (2008) Physical setting and tephrochronology of the summit caldera ice record at Mount Moulton, West Antarctica. *Geological Society of America Bulletin* **120**(7-8), 796-812.
- Eberts S.M., Bohlke J.K., Kauffman L.J., and Jurgens B.C. (2012) Comparison of particle-tracking and lumped-parameter age-distribution models for evaluating vulnerability of production wells to contamination. *Hydrogeology J.* **20**, 263-282.
- Ekwrzel B., Schlosser P., Smethie W., Jr., Plummer L. N., Busenberg E., Michel R. L., Weppernig R. and Stute M. (1994) Dating of shallow groundwater—Comparison of the transient tracers $^3\text{H}/^3\text{He}$, chlorofluorocarbons and ^{85}Kr . *Water Resources Research* **30**, 1693-1708.
- Giggenbach, W. F. (1992) Isotopic shifts in waters from geothermal and volcanic systems along convergent plate boundaries and their origin. *Earth and Planetary Science Letters* **113**, 495-510.
- Gilfillan S. et al. (2008). The noble gas geochemistry of natural CO_2 gas reservoirs from the Colorado Plateau and Rocky Mountain provinces, USA. *Geochimica et Cosmochimica Acta* **72**(4), 1174–1198.
- Gilfillan S. M. V. et al. (2009) Solubility trapping in formation water as dominant CO_2 sink in natural gas fields. *Nature*, **458**(7238), 614–8.
- Green C.T., Bohlke J.K., Bekins B. and Phillips S. (2010) Mixing effects on apparent reaction rates and isotope fractionation during denitrification in a heterogeneous aquifer. *Water Res. Res.* **46**, 1-19.
- Hilton D. R., Fischer T. P. and Marty B. (2002) Noble gases in subduction zones and volatile recycling. In: D. Porcelli, C. Ballentine, R. Wieler (eds.), *MSA Special Volume: Noble Gases in Geochemistry and Cosmochemistry*. **47**, 319-362.
- Hiyagon H. and Kennedy B. M. (1992). Noble gases in CH_4 -rich gas fields, Alberta, Canada. *Geochim. Cosmochim. Acta* **56**, 1569–1589.
- Holzer M. and Primeau F. W. (2010) Improved constraints on transit time distributions from argon-39: A maximum entropy approach, *J. Geophys. Res.* **115**, C12021, 10.1029/2010jc006410, 2010.
- Jenk T. M., Szidat S., Schwikowski M., Gäggeler H. W., Wacker L., Synal H. A. and Saurer M. (2007) Microgram level radiocarbon (^{14}C) determination on carbonaceous particles in ice, *Nucl. Instrum. Meth. B* **259**(1), 518-525.
- Jiang W. et al. (2011) Ar-39 Detection at the 10^{-16} Isotopic Abundance Level with Atom Trap Trace Analysis. *Phys. Rev. Lett.* **106**, 103001.
- Jiang W. et al. (2012) An Atom Counter for Measuring ^{81}Kr and ^{85}Kr in Environmental Samples. *Geochim. Cosmochim. Acta* **91**, 1-6.
- Jouzel J. et al. (2007) Orbital and millennial Antarctic climate variability over the past 800,000 years, *Science*, **317**(5839), 793-796.
- Kennedy B. M., Reynolds J., Smith S. and Truesdell A. (1987) Helium Isotopes: Lower geyser basin, Yellowstone National Park. *Journal of Geophysical Research*, **92**(B12), 12477–12489.

- Kennedy B. M., Torgersen T. and van Soest M. (2002) Multiple atmospheric noble gas components in hydrocarbon reservoirs: a study of the Northwest Shelf, Delaware Basin, SE New Mexico. *Geochim. Cosmochim. Acta*, **66**(16), 2807–2822.
- Kropf S. (1996) Bestimmung der Altersverteilung junger Grundwässer mit Hilfe des Edelgasisotops ^{85}Kr und Tritium. Diplomarbeit, Universität Bern.
- Lal D., Jull A. J. T., Donahue D. J., Burtner D. and Nishiizumi K. (1990) Polar ice ablation rates measured using insitu cosmogenic C-14, *Nature* **346**(6282), 350-352.
- Lehmann B. E., Davis S. N. and Fabryka-Martin J. T. (1993) Atmospheric and subsurface sources of stable and radioactive nuclides used for groundwater dating. *Water Res. Res.* **29**, 2027-2040.
- Lehmann B. E. and Purtschert R. (1997) Radioisotope dynamics – the origin and fate of nuclides in groundwater. *Appl. Geochem.* **12**, 727-738.
- Lehmann B. E. et al. (2003) A comparison of groundwater dating with ^{81}Kr , ^{36}Cl and ^4He in 4 wells of the Great Artesian Basin, Australia. *Earth Planetary Sci. Lett.* **212**, 237-250.
- Loosli H. H. and Oeschger H. (1968) Detection of ^{39}Ar in atmospheric Ar. *Earth Planet. Sci. Lett.* **5**, 191-198.
- Loosli H. H. and Oeschger H. (1969) ^{37}Ar and ^{81}Kr in the atmosphere. *Earth Planet. Sci. Lett.* **7**, 67-71.
- Loosli H. H. (1983) A dating method with ^{39}Ar . *Earth and Planetary Science Letters* **63**, 51-62.
- Loosli H., Moell M., Oeschger H., and Schotterer U. (1986) Ten years low-level counting in the underground laboratory in Bern, Switzerland. *Nucl. Instrum. Meth. B* **17**, 402-405.
- Loosli, H. H. (1989) Argon-39: A tool to investigate ocean water circulation and mixing, in: *Handbook of Environmental Isotope Geochemistry, Vol. 3. The Marine Environment*, edited by: Fritz, P., and Fontes, J. C., Elsevier Science Publishers, Amsterdam.
- Loosli H., Lehmann B. and Balderer W. (1989) Argon-39, argon-37 and krypton-85 isotopes in Stripa groundwaters. *Geochim. Cosmochim. Acta* **53**, 1825-1829.
- Loosli H., Lehmann B. E. and Smethie W. R. (1999) Noble gas radiotopes (^{37}Ar , ^{85}Kr , ^{39}Ar , ^{81}Kr). In *Environmental Tracers in Subsurface Hydrology* (ed. P. G. Cook and A. L. Herczeg), pp. 379-396. Kluwer.
- Loosli H. H. and Purtschert R. (2005) Rare Gases. In *Isotopes in the Water Cycle: Past, Present and Future of a Developing Science* (ed. P. Aggarwal, J. R. Gat, and K. Froehlich), pp. 91-95. IAEA.
- Marty B. (1989) Neon and xenon isotopes in MORB: implications for the earth-atmosphere evolution. *Earth Planet. Sci. Lett.* **94**, 45.
- Marty, B. and Dauphas, N. (2003) The nitrogen record of crust-mantle interaction and mantle convection from Archean to Present. *Earth Planet. Sci. Lett.* **206**, 397-410.
- Marty, B. and Tolstikhin, I. N. (1998) CO₂ fluxes from mid-ocean ridges, arcs and plumes. *Chem. Geol.* **145**, 233-248.
- Matsumoto K. (2007) Radiocarbon-based circulation age of the world oceans. *J. Geophys. Res.* **112**, Artn C09004. Doi 10.1029/2007jc004095.
- Matsumoto T., Han L.-F., Jaklitsch M. and Aggarwal P.K. (2012) A portable membrane contactor sampler for measuring noble gas concentrations and isotope ratios in groundwater. *Groundwater* (in press).
- Mei D.-M., Yin Z.-B., Spaans J., Koppang M., Hime A., Keller C., and Gehman V. M. (2010) Prediction of underground argon content for dark matter experiments. *Phys. Rev. C* **81**, 055802.
- Momoshima N., Inoue F., Ohta T., Mahara Y., Sugihara S., Shimada J. and Taniguchi M. (2011) Application of ^{85}Kr dating to groundwater in volcanic aquifer of Kumamoto Area, Japan. *J. Radioanal. Nucl. Chem.* **287**, 761.
- Oeschger H. (1987) Accelerator mass spectrometry and ice core research. *Nucl. Instrum. Meth. B* **29**, 196-202.
- Ohta T., Mahara Y., Momoshima N., Inoue F., Shimada J., Ikawa R. and Taniguchi M. (2009) Separation of dissolved Kr from a water sample by means of a hollow fiber membrane. *Journal of Hydrology*; doi:10.1016/j.jhydrol.2009.07022.
- Park J., Bethke C. M., Torgersen T. and Johnson T. M. (2002) Transport modeling applied to the interpretation of groundwater ^{36}Cl age. *Water Resources Research* **38**, 1043.
- Petrenko, V. V., Severinghaus J. P., Brook E. J., Reeh N. and Schaefer H. (2006) Gas records from the West Greenland ice margin covering the Last Glacial Termination: a horizontal ice core, *Quat. Sci. Rev.* **25**(9-10), 865-875.
- Phillips F. (2000) Chlorine-36. In *Environmental Tracers in Subsurface Hydrology* (ed. P. G. Cook and A. L. Herczeg), pp. 379-396. Kluwer Academic Publishers, Boston.
- Pinti D. L. and Marty B. (1995). Noble gases in crude oils from the Paris Basin, France: Implications for the origin of fluids and constraints on oil-water-gas interactions. *Geochimica et Cosmochimica Acta*, **59**(16), 3389–3404.
- Plummer L. N., Michel R. L., Thurman E. M. and Glynn P. D. (1993) Environmental tracers for age-dating young ground water: In, Alley, W.M., ed., *Regional Ground-Water Quality*, Chap. 11, Van Nostrand Reinhold, New York, p. 255-294.

- Plummer L. N. and Sprinkle C. L. (2001) Radiocarbon dating of dissolved inorganic carbon in groundwater from confined parts of the Upper Floridan aquifer, Florida, USA. *Hydrogeology Journal* **9**, 127-150.
- Probst P. C., Yokochi R. and Sturchio N. C. (2007) Method for Extraction of Dissolved Gases From Groundwater for Radiokrypton Analysis. *4th Mini Conference on Noble Gases in the Hydrosphere and in Natural Gas Reservoirs*.
- Riedmann R. (2011) Separation of Argon from atmospheric air and measurements of ^{37}Ar for CTBT purposes. PhD dissertation, University of Bern, pp. 272.
- Sano Y. and Wakita H. (1985) Geographical distribution of $^3\text{He}/^4\text{He}$ ratios in Japan: Implications for arc tectonics and incipient magmatism. *J. Geophys. Res.* **90**, 8729–8741.
- Sano Y. and Fischer, T. P. (2012) The analysis and interpretation of noble gases in modern hydrothermal systems. In: *Noble Gases as Geochemical Tracers (Peter Burnard, editor). Series: Advances in Isotope Geochemistry (J. Hoefs, series editor). ISBN 978-3-642-28835-7 Springer Verlag, Heidelberg.*
- Schlosser P., Stute M., Dorr H., Sonntag C. and Munnich K. O. (1988) Tritium/ ^3He dating of shallow groundwater. *Earth and Planetary Science Letters* **89**, 353-362.
- Schlosser P., Kromer B., Weppernig R., Loosli H.H., Bayer R., Bonani G. and Suter M. (1994a) The distribution of ^{14}C and ^{39}Ar in the Weddell Sea. *J. Geophys. Res.* **99**, 10,275-10,287.
- Schlosser P., Kromer B., Östlund H.G., Ekwurzel B., Bönisch G., Loosli H.H., and Purtschert R. (1994b) On the distribution of ^{14}C and ^{39}Ar in the Arctic Ocean: implications for deep water formation. *Radiocarbon*, **36**, 327-343.
- Shaw A. M., Hauri E., Fischer T. P., Hilton D. R. and Kelley K. A. (2008) Hydrogen isotopes in Mariana arc melt inclusions: Implications for subduction dehydration and the deep-Earth water cycle. *Earth and Planet. Sci. Lett.* **272**, 138-145.
- Sinisalo A. and Moore J. C. (2010) Antarctic blue ice areas - towards extracting palaeoclimate information, *Antarct. Sci.*, **22**(2), 99-115.
- Smethie Jr. M. and Mathieu G. (1986) Measurement of Krypton-85 in the Ocean. *Marine Chemistry* **18**, 17-33.
- Smethie Jr. M., Solomon D. K., Schiff S. L. and Mathieu G. G. (1992) Tracing groundwater flow in the Borden Aquifer using ^{85}Kr . *J. Hydrology* **130**, 279-297.
- Sturchio N. C. et al. (2004) One million year old groundwater in the Sahara revealed by krypton-81 and chlorine-36. *Geophys. Res. Lett.* **31**(5), L05503.
- Taran, Y. A., Pokrovsky, B. G., and Dubik, Y. M. (1989) Isotopic composition and the origin of water from andesitic magmas. *Trans.Ac.Sci.,USSR* **304**, 440-443.
- Tatsumi, Y. (1989) Migration of fluid phases and genesis of basalt magmas in subduction zones. *J. of Geophys. Res.* **94**, 4697-4707.
- Torgersen T. and Clarke W. B. (1985) Helium accumulation in groundwater, I: An evaluation of sources and the continental flux of crustal ^4He in the Great Artesian Basin, Australia. *Geochimica et Cosmochimica Acta* **49**, 1211-1218.
- Turkevitch A., Winsberg L., Flotow H. and Adams R. M. (1997) The radioactivity of atmospheric krypton in 1949-1950. *Proc. Natl. Acad. Sci.* **94**, 7807-7810.
- Wallace P. J. (2005) Volatiles in subduction zone magmas: concentrations and fluxes based on melt inclusion and volcanic gas data. *Journal of Volcanology and Geothermal Research* **140**, 217-240.
- Weiss W. A., Sartorius H. and Stockurger H. (1989) *Proc. Consultant Meeting on Isotopes of Noble Gases as Tracers in Environmental Studies*, pp. 29-72. Vienna: IAEA.
- Welte J., Ritterbusch F., Steinke I., Henrich M., Aeschbach-Hertig W. and Oberthaler M. K. (2010) Toward the realization of atom trap trace analysis for ^{39}Ar . *New J. Phys.* **12**, 065031.
- Wiesler F. (1996) Membrane Contactors: An introduction to the technology. www.liqui-cel.com.
- Winger K., Feichter F., Klinowski M. B., Sartorius H. and Schlosser H. (2005) A new compilation of the atmospheric krypton-85 inventories from 1945 to 2000 and its evaluation in a global transport model. *J. of Environ. Rad.* **80/2**, 183-215.
- Yokochi R., Heraty L. J. and Sturchio N. C. (2008) Method for Purification of Krypton from Environmental Samples for Analysis of Radiokrypton Isotopes. *Analytical Chemistry* **80**(22), 8688–8693.
- Yokochi R., Sturchio N. and Purtschert R. (2012a). Determination of crustal fluid residence times using nucleogenic ^{39}Ar . *Geochimica et Cosmochimica Acta* **88**, 19–26.
- Yokochi R., Sturchio N.C., Purtschert R., Jiang W, Lu Z.-T., Mueller P., Yang G.-M., Kennedy B. M. and Kharaka Y. (2012b) Noble Gas Radionuclides in Yellowstone Geothermal Gas Emissions: A Reconnaissance. *Under revision for Chemical Geology (Special Issue: Frontiers in Gas Geochemistry)*.

Appendix A. TANGR2012 Participants

Jun	Abrajano	National Science Foundation
Werner	Aeschbach-Hertig	University of Heidelberg
Pradeep	Aggarwal	International Atomic Energy Agency
Jorge	Alvarado	Argonne National Laboratory
Henning	Back	Princeton University
John Karl	Bohlke	U. S. Geological Survey
Christo	Buizert	Oregon State University
Kyle	Cronin	University of Illinois at Chicago
Andrew	Davis	University of Chicago
Hillary	Dugan	University of Illinois at Chicago
Paul	Fenter	Argonne National Laboratory
Tobias	Fischer	University of New Mexico
Ronny	Friedrich	Lamont-Doherty Earth Observatory
Karl	Haase	U. S. Geological Survey
Dave	Hofman	University of Illinois at Chicago
Mark	Holzer	University of New South Wales
Wei	Jiang	Argonne National Laboratory
Mack	Kennedy	Lawrence Berkeley National Laboratory
Rolf	Kipfer	EAWAG: Swiss Federal Institute of Aquatic Science & Technology
Markus	Kohler	University of Hamburg
Walter	Kutschera	University of Vienna
Andrew	Loose	Columbia University
Andy	Love	Flinders University
Zheng-Tian	Lu	Argonne National Laboratory
Kevin	Mandernack	Indiana-Purdue University
Jennifer	McIntosh	University of Arizona
Bob	Michel	U. S. Geological Survey
Peter	Mueller	Argonne National Laboratory
Thomas M.	Parris	Kentucky Geological Survey, University of Kentucky
Roland	Purtschert	University of Bern
Laura	Rademacher	University of the Pacific
Gulshan	Rai	Department of Energy
Florian	Ritterbusch	Heidelberg University
Yuji	Sano	University of Tokyo
Peter	Schlosser	Lamont-Doherty Earth Observatory
Jeff	Severinghaus	Scripps Institution of Oceanography
William	Smethie	Lamont-Doherty Earth Observatory
Douglas Kip	Solomon	University of Utah
Neil	Sturchio	University of Illinois at Chicago
Martin	Stute	Lamont-Doherty Earth Observatory
Toste	Tanhua	University of Keil
Gisela	Winckler	Lamont-Doherty Earth Observatory
Eugene	Yan	Argonne National Laboratory
Reika	Yokochi	University of Chicago

Appendix B. TANGR2012 Agenda

Thursday, June 21

Chair: Zheng-Tian Lu

- 08:45 Purtschert Passing in review of radio-noble-gas measurements by low level counting
09:30 Kutschera Atom counting of noble gas radioisotopes with accelerators: successes and limitations

Chair: Andrew Davis

- 10:15 Lu Atom Trap Trace Analysis
10:45 Jiang ATTA: 81Kr and 85Kr at USTC
11:00 Mueller ATTA: 39Ar at Argonne
11:15 Ritterbusch ATTA: 39Ar at Heidelberg – The atom optical aspect
11:30 Aeschbach-Hertig ATTA: 39Ar at Heidelberg – Preparation of water and ice samples

Chair: JK Bohlke

- 13:30 Sturchio Applications of 81Kr and 85Kr in groundwater hydrology
14:00 Aggarwal Global groundwater age determination – IAEA perspective
14:30 Kipfer Noble gases in unconventional aquatic systems

Chair: Mack Kennedy

- 15:15 Fischer Constraints on the deep water cycle based on volcanic and hydrothermal gas emissions
15:45 Yokochi Tracing time scales of fluid residence and migration in the crust

Friday, June 22

Chair: Yuji Sano

- 08:30 Schlosser 39Ar measurements in the polar oceans
09:00 Smethie 39Ar measurements in the Atlantic and Pacific oceans
09:30 Holzer Improved constraints on transit time distribution from 39Ar: a maximum entropy approach

Chair: Gisela Winckler

- 10:15 Severinghaus Atmospheric krypton and xenon from ice cores suggest a two degree deep ocean warming from 18 ka to 16 ka
10:45 Buizert Radiometric dating of ancient glacial ice using 81Kr
11:15 Love Dating old groundwater by multiple tracers including 81Kr
11:45 Winckler Thoughts on dating old Antarctic ice

13:30 Group Discussion
14:30 Summary
16:00 End

Posters

- Loose ATTA Device for Measuring Trace Krypton Contamination in Xe Dark Matter Detectors
Suknik Optical Production of Metastable Krypton
Parris Fluid Evolution in Cambrian-Ordovician Knox Group Reservoir
Kohler ATTA at Hamburg – Initial Experience in the Optical Production of Metastable Krypton