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Tracer applications of noble gas radionuclides in the geosciences

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ABSTRACT

Noble gas radionuclides, including ^{81}Kr ($t_{1/2}$ = 229,000 years), ^{85}Kr ($t_{1/2}$ = 10.8 years), and ^{39}Ar ($t_{1/2}$ = 269 years), possess nearly ideal chemical and physical properties for studies of earth and environmental processes. Recent advances in Atom Trap Trace Analysis (ATTA), a laser-based atom counting method, have enabled routine measurements of the radiokrypton isotopes, as well as the demonstration of the ability to measure ^{39}Ar in environmental samples. Here we provide an overview of the ATTA technique, and a survey of recent progress made in several laboratories worldwide. We review the application of noble gas radionuclides in the geosciences and discuss how ATTA can help advance these fields, specifically: determination of groundwater residence times using ^{81}Kr, ^{85}Kr, and ^{39}Ar; dating old glacial ice using ^{81}Kr; and an ^{39}Ar survey of the main water masses of the oceans, to study circulation pathways and estimate mean residence times. Other scientific questions involving a deeper circulation of fluids in the Earth's crust and mantle are also within the scope of future applications. We conclude that the geoscience community would greatly benefit from an ATTA facility dedicated to this field, with instrumentation for routine measurements, as well as for research on further development of ATTA methods.

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1. Introduction

Due to their inert behavior in natural systems, noble gas nuclides have been used for many decades in the earth sciences (Porcelli et al., 2002). They provide fundamental information on mass budgets and exchange, as well as mean residence times in the hydrosphere (oceans, lakes, and groundwater), the atmosphere, the geosphere, and the cryosphere. While the stable nuclides of noble gases can be measured routinely with high precision using mass spectrometry, the radioactive nuclides of noble gases in natural samples are rare and very difficult to measure with sufficient precision. The radionuclides, including ^{81}Kr (half-life, $t_{1/2}$ = 229,000 years), ^{85}Kr ($t_{1/2}$ = 10.8 years), and ^{39}Ar ($t_{1/2}$ = 269 years), possess nearly ideal chemical and physical properties for studies of earth and environmental processes. In practice, however, few studies have been able to utilize these tracers because of the large sample sizes and the complex analytical systems required for measuring their extremely low isotopic abundances (10^{-11}–10^{-16}). Low-level radioactive decay counting is applied to the analysis of ^{39}Ar and ^{85}Kr, but is not possible for ^{81}Kr due to its low activity. Various atom-counting methods have been pursued over the past four decades, including efforts focused on Accelerator Mass Spectrometry (AMS) (Collon et al., 2004).

The advent of ATTA (Atom Trap Trace Analysis) (Jiang et al., 2012; Yang et al., 2013) in principle enables routine measurements of rare noble gas isotopes and thus has reignited the discussion among Earth scientists about how to best apply these valuable tracers to compelling scientific problems. In the first Workshop on Tracer Applications of Noble-Gas Radionuclides (TANGR2012), held at Argonne National Laboratory in June, 2012, the attendees reviewed past applications of these tracers in the field of Earth science and projected future needs. The scientific findings are summarized in this article. Additional materials are available at the workshop website, http://www.phy.anl.gov/events/tangr2012/.

After a brief overview of the relevant noble gas radionuclides, we describe the ATTA method and specific experimental instruments. We then discuss suitable methods for noble gas sample collection and purification. These method- and technique-oriented chapters are followed by a discussion of the applications of ^{85}Kr, ^{39}Ar and ^{81}Kr in the hydrosphere (oceans and groundwater), cryosphere and geosphere. The Conclusions section projects the trajectories for the field of applying noble gas radionuclides to earth and environmental sciences, and recommends concrete pathways towards more widespread use of these isotopes in the geosciences.

2. Noble gas radionuclides

There are three long-lived ($t_{1/2}$ > 1 years) noble-gas radionuclides with tracer applications in the environment: ^{81}Kr ($t_{1/2}$ = 229,000 years), ^{85}Kr (10.8 years), and ^{39}Ar (269 years). 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}Kr/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}Kr/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 (Turkevitch et al., 1997; Ahlswede et al., 2013). The atmospheric ^{85}Kr/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}Kr/Kr in the northern hemisphere, where most of the nuclear fuel reprocessing plants reside, can be ~ 20% higher than that in the southern hemisphere (Weiss et al., 1989). ^{85}Kr is useful for dating young (1–40 years) groundwater (Smethie Jr. 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 (Jiang et al., 2012; Yang et al., 2013).

^{39}Ar conveniently fills an apparent age gap (Fig. 1) between ^{85}Kr and ^{3}H/^{3}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}Ar/Ar ratio of 8×10^{-16} (Loosli, 1983). There can be substantial subsurface production in granite rocks through the ^{39}K(n, p)^{39}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, for example, by simultaneous measurements of ^{37}Ar ($t_{1/2}$ = 35 d) produced by neutron-activation of ^{40}Ca. In ocean water, *in situ* production of ^{39}Ar is not significant. However, atmospheric ^{39}Ar dissolved in ocean water is a useful chronometer for tracing ocean circulation and ventilation. At present, LLC is used for ^{39}Ar (and ^{37}Ar) analysis, but it requires 1–2 tons of water per sample. The ATTA instruments have been used to measure ^{39}Ar/Ar in environmental samples on much smaller amounts of Ar than those required for LLC (Jiang et al., 2011).

3. Atom Trap Trace Analysis

Atom Trap Trace Analysis (ATTA) is a laser-based atom counting method (Chen et al., 1999). A magneto-optical trap is used to capture

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