What trapped atoms reveal about global groundwater

Zheng-Tian Lu

Atom-trap trace analysis can reliably detect age-revealing noble-gas isotopes whose isotopic abundances are as low as 1 part in 10^{16}.

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Radioactive carbon-14 is well known as a tool for dating archaeological samples, but it is hardly the only radioisotope useful for establishing age. As panel a in the figure shows, several isotopes, including ones of the noble gases argon and krypton, allow for the dating of samples over many orders of magnitude in age.

The dream of radiokrypton dating began in 1969. In that year Heinz Hugo Loosli and Hans Oeschger of the University of Bern detected the decay of natural ^{81}Kr in krypton gas extracted from air. The isotope, whose half-life is 230 000 years, is produced in the upper atmosphere by cosmic-ray-induced spallation (nuclear fragmentation) and neutron activation of stable krypton. It remains in the atmosphere for a long time and thus has a uniformly distributed isotopic abundance—about 6 parts in 10^{13}. A few percent of atmospheric krypton, including ^{81}Kr, dissolves in water or is trapped in ice, and thus the radioisotope can trace environmental samples. With few exceptions, there appear to be no other significant sources of ^{81}Kr (even counting human-induced nuclear fission), and radioactive decay is the only significant sink; the isotope is well suited for radiodating. Indeed, ^{81}Kr is an ideal tracer for dating water and ice having an age of 10^5–10^6 years—that is, water and ice that was in contact with the atmosphere 10^5–10^6 years ago. That range is beyond the reach of ^{14}C dating.

Physicists have pursued radiokrypton dating with a variety of approaches. For example, in 2000 Walter Kutschera of the University of Vienna and his collaborators first demonstrated ^{81}Kr dating of old groundwater (having an age of more than 10^5 years) with an innovative form of accelerator mass spectrometry. In that technique, a GeV-energy, football-field-sized accelerator separates isotopes based on charge and mass differences. By late 2011 researchers had conducted proof-of-principle measurements on about a dozen environmental samples, but a practical method capable of routine analysis remained elusive. Then an instrument called ATTA-3 began operation at Argonne National Laboratory. Named after the atom-trap trace analysis method that my colleagues and I have been developing during the past 15 years, ATTA-3 has helped to date some 10 samples per month, with each sample extracted from about 200 liters of water or 100 kilograms of ice. The third-generation instrument is opening up new research avenues, and the new understandings it enables should have implications, in particular, for climate change analysis and water-resource management.

In addition to ^{81}Kr, Earth's atmosphere includes two other long-lived noble-gas isotopes with tracer applications: ^{85}Kr, with a half-life of 10.8 years and an atmospheric isotopic abundance of 1 part in 10^{11}, and ^{39}Ar, with a half-life of 269 years and an atmospheric abundance of 8 parts in 10^{16}. Krypton-85 is produced in nuclear fission and released into the atmosphere primarily by nuclear-fuel reprocessing plants. Atmospheric ^{39}Ar, like ^{81}Kr, is produced by cosmic-ray-induced spallation or neutron activation. Each of the isotopes covers a geologically useful age range, and each can be analyzed with ATTA-3.

Counting atoms with a laser trap

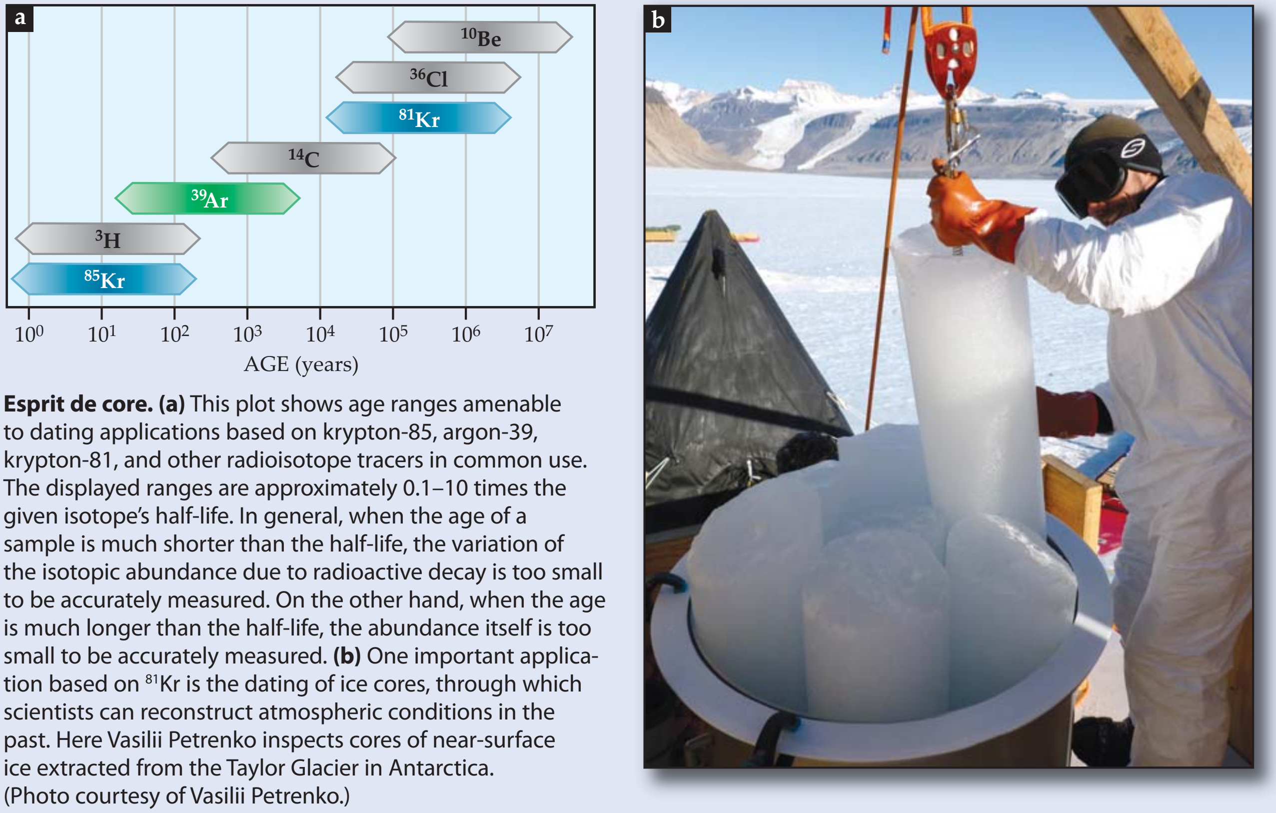
Atom-trap trace analysis involves a trap, formed by six laser beams, that captures an atom of a particular isotope. When the laser frequency matches an excitation energy of the desired species, atoms of that type—and only atoms of that type—interact with the laser beams strongly enough to be trapped. A trapped atom continuously scatters photons from the laser beams and appears as a bright dot that can be detected with a CCD camera. Repeated resonant excitations make the detection process highly redundant and guarantee that the identification of the targeted isotope is never in error.

Cross-sample contamination remains the primary limitation on both sample size and processing time when ATTA-3 is applied to analyze samples that include krypton. Laser trapping requires that the krypton atoms first be excited to a metastable level, a step that presently occurs in a gas discharge. Unfortunately, the discharge also ionizes the atoms and implants them into surrounding walls; those implanted atoms can leak into and contaminate subsequent samples. With future advances in bright vacuum UV light sources, the discharge step could be replaced with a photon excitation scheme that would mitigate the cross-contamination and reduce the required sample size.

In addition to krypton isotopes, ATTA-3 can analyze ^{39}Ar/Ar ratios in environmental samples. In our experiments, my colleagues and I found that we could exclude the possibility of interference from other atomic or molecular species at levels of 1 part in 10^{16}. However, the isotopic abundance of ^{39}Ar is extremely low, 1/1000 that of ^{81}Kr, and we only counted an average of six ^{39}Ar atoms per day. That rate will need to be increased by a factor of 10–100 if ^{39}Ar dating is to be implemented for practical applications such as are described in the following section. Isotope pre-enrichment and other techniques will help get the counting rate up.

A world of opportunity

Last summer Argonne National Laboratory hosted the first International Workshop on Tracer Applications of Noble-Gas Radionuclides. Topics ranged from glaciology to volcanology. Here I'll review some highlights of the discussions; full



Esprit de core. (a) This plot shows age ranges amenable to dating applications based on krypton-85, argon-39, krypton-81, and other radioisotope tracers in common use. The displayed ranges are approximately 0.1–10 times the given isotope's half-life. In general, when the age of a sample is much shorter than the half-life, the variation of the isotopic abundance due to radioactive decay is too small to be accurately measured. On the other hand, when the age is much longer than the half-life, the abundance itself is too small to be accurately measured. **(b)** One important application based on ^{81}Kr is the dating of ice cores, through which scientists can reconstruct atmospheric conditions in the past. Here Vasilii Petrenko inspects cores of near-surface ice extracted from the Taylor Glacier in Antarctica. (Photo courtesy of Vasilii Petrenko.)

presentations and more are available at the workshop website, http://www.phy.anl.gov/events/tangr2012.

Polar ice cores help geologists reconstruct Earth's past climate and atmospheric composition as far back as 800 000 years. Old ice can be obtained from deep ice cores, but near-surface areas exposed to ablation can also present old samples and potentially provide an alternative to deep ice coring for paleoclimate studies. A team comprising glaciologists and physicists (including our group) has used ATTA-3 to test the feasibility and accuracy of ^{81}Kr dating of old ice by analyzing samples from the Taylor Glacier in Antarctica (see panel b of the figure); ages of the samples were also determined by stratigraphy.

Ocean circulation is a major component of Earth's dynamic climate system. The typical time scale for regional ocean circulation is comparable to the half-life of ^{39}Ar, and for that reason, ^{39}Ar dating can potentially help scientists map ocean currents with improved resolution. A systematic survey of dissolved ^{39}Ar throughout the oceans, particularly when combined with ^{14}C data, will fill major gaps in our knowledge of deep-ocean circulation and mixing. It will also enable oceanographers to devise more accurate predictions of oceanic sequestration of atmospheric carbon dioxide.

Radiodating with noble-gas isotopes has already led to advances in hydrology. On the surface where gases are exchanged between air and water, the isotopic abundance of a dissolved gas is equal to its atmospheric value. As water flows down from the surface, it gets older and abundances of radioisotopes decrease due to nuclear decay. By measuring the ages of water samples extracted from a network of wells, hydrologists can map the underground migration of water and so better understand—perhaps even predict—how an aquifer will respond to natural or human-made disturbances such as water pumping. The resulting models can aid in managing water resources.

Using the ATTA technique to take measurements of ^{81}Kr from the Nubian Aquifer of Africa, the Great Artesian Basin of Australia, and the Guarani Aquifer of South America has provided useful input for hydrodynamic models and has helped validate such models and measurements made with helium-4 and chlorine-36 tracers. Hydrologists are planning more extensive sampling on major aquifer systems worldwide. Furthermore, ^{81}Kr dating verified the isolation of groundwater near the Waste Isolation Pilot Plant, a nuclear-waste storage site in New Mexico.

Shallow, "young" groundwater less than 60 years old is commonly traced via hydrogen-3 or chlorofluorocarbons, but ^{85}Kr provides a valuable alternative. When combined with those common tracers, ^{85}Kr data will help scientists to better assess the flow of the groundwater and its susceptibility to chemical contamination. As ATTA is further developed, ^{39}Ar dating may become a standard tool for scientists evaluating groundwater resources. The argon isotope is especially valuable because it addresses the critical 100- to 1000-year time range that is presently not well resolved by other tracers.

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Additional resources

▶ Z.-T. Lu, "Atom trap, krypton-81, and global groundwater," plenary presentation at the American Physical Society 2012 April meeting, online at http://absuploads.aps.org/presentation.cfm?pid=10371.

▶ W. Jiang et al., "An atom counter for measuring ^{81}Kr and ^{85}Kr in environmental samples," *Geochim. Cosmochim. Acta* **91**, 1 (2012).

▶ W. Jiang et al., "^{39}Ar detection at the 10^{-16} isotopic abundance level with atom trap trace analysis," *Phys. Rev. Lett.* **106**, 103001 (2011). ■