



MEASURING NOBLE GASES FOR THERMOCHRONOLOGY

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DOI: 10.2138/gselements.16.5.343

The articles in this issue show how applications of noble gas thermochronology can help answer fundamental questions about Earth and planetary processes. Here, we discuss how noble gas measurements are actually made. We review the different methods used to extract and isolate noble gases from natural materials and to measure those gas concentrations and isotopic compositions using mass spectrometry.

NOBLE GAS EXTRACTION AND ISOLATION

To extract gases from rocks and minerals in the laboratory, we often take advantage of the same properties that make them useful for thermochronology: they diffuse with an exponential dependence on temperature, and they are highly incompatible elements. Heating rocks and minerals to high temperatures in an ultrahigh vacuum ($<10^{-9}$ torr) liberates noble gases, either by diffusion in stable phases or through melting. In the early days, this heating was usually by radiofrequency induction, but labs turned to double-vacuum resistance furnaces that isolate the sample vacuum from the vacuum surrounding the heating element, reducing exposure of the sample to gases sourced from heated metal. Today, heating and extraction with a laser is also very common. Laser heating typically adds a lower background signal than furnaces because lasers heat a smaller volume, and they have become cheaper and easier to work with. Lasers can either couple directly with rocks and minerals to achieve heating or can heat samples indirectly by coupling with metal packets holding sample material (e.g., House et al. 2000; see title image in Gautheron and Zeitler 2020 this issue). An advantage of both furnace and indirect laser heating is that they can be used to control sample temperatures accurately and precisely, which is necessary for quantifying the kinetics of noble gas diffusion. However, conducting such measurements can be technically challenging and does require care in experimental design. A less frequently used way to extract noble gases is laser ablation, whereby the surface of a sample is removed (ablated) with a high-energy, short-wavelength laser pulse (e.g., Boyce et al. 2006). This approach can be used to extract noble gases from a targeted subregion of a mineral or rock, but is often challenging because, in most minerals, small ablated volumes release proportionately small amounts of noble gases.

These extraction methods liberate not only noble gases but also other gases and other easily volatilized elements that can be a nuisance during noble gas measurement, introducing mass interferences or altering sensitivity through gas scattering or changes in sample ionization. We typically “clean” the extracted gas prior to measurement on a mass spectrometer using reactive-metal getter pumps and sometimes cold traps that separate gas species based on their adsorption properties and freezing temperatures. By the same principle, cold traps can also be used to separate different noble gas elements from one another, allowing for multiple noble gases to be measured in sequence from the same aliquot of gas.

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NOBLE GAS MEASUREMENT

Having extracted clean gas, we can then analyze its composition using a mass spectrometer. There are three essential parts of a mass spectrometer: an ion source, a mass analyzer, and detectors.

Ionization

All noble gas ion sources operate by using electron impact to strip an electron from a noble gas atom. In this process, electrons are generated from a hot metal filament, then accelerated by an electric field, which creates a stream of electrons that travels from the filament, across the ionizing chamber and into an electron trap. The filament emission and trap current are closely controlled using feedback in order to create an extremely stable beam. Such sources cleverly use a pair of magnets to cause this electron beam to spiral, greatly increasing the electrons' path length and, hence, their chance of intersecting noble gas atoms. Intersected atoms are stripped of one or more of their electrons, generating a positively charged noble gas ion. A number of charged metal plates are then used to collimate and focus the ions and accelerate them into the mass analyzer across a potential of several kilovolts. Measurement parameters, such as peak shape and mass-spectrometer sensitivity, will vary as a function of the voltages on these different plates as well as on the energy of the electrons emitted from the source filament (e.g., Mabry et al. 2012).

A major difference between analyses for noble gases compared to other gas species is that their small, finite sample sizes means measurement must be done in a static vacuum: all the gas is let into the mass spectrometer at once while the machine is isolated from the ion and the turbomolecular pumps that maintain its ultrahigh vacuum. Once introduced, the noble gas atoms in the mass spectrometer will be continuously ‘consumed’ by ionization, then implanted into the detectors, flight tube, or ion source itself. As a result, the strength of the observed ion beam will decrease as a function of time for large beams, but could even increase for small beams if previously embedded sample gas is liberated from surfaces. Because each individual beam changes in intensity during analysis, the beam intensity must be quantified. To do this, we typically extrapolate the trend in measured ion-beam intensity to “time zero,” the time when the gas first entered the mass spectrometer.

Mass-to-Charge Ratio Separation

Once noble gases are ionized, we use a mass analyzer to separate different noble gas isotopes from one another. Two different types of mass analyzer are commonly used in noble gas mass spectrometry: magnetic sectors, and quadrupoles (FIG. 1). In a magnetic sector, ions are accelerated into a magnetic field generated by a strong electromagnet that has the shape of a “sector” of a circle (FIG. 1A). The ions enter the magnetic field nearly perpendicular to magnetic field lines, which deflect them into circular paths. Heavier ions take a wider path, segregating ions with different mass-to-charge ratios into separated ion beams as they exit the magnetic field (FIG. 1A). In a machine with a single detector, it is then possible to measure the ion beam for each mass by precisely shifting the magnetic field.

In contrast to a magnetic sector, a quadrupole consists of four cylindrical metal rods arranged in a rectangle (FIG. 1B). One pair of diagonally opposite rods is kept at one voltage, while the other pair is held at the opposite voltage. A combination of radiofrequency (RF) and direct current (DC) voltages are applied to each pair of rods to generate a two-dimensional, hyperbola-shaped electric field. The field only allows ions with a narrow range of mass-to-charge ratio to travel down the

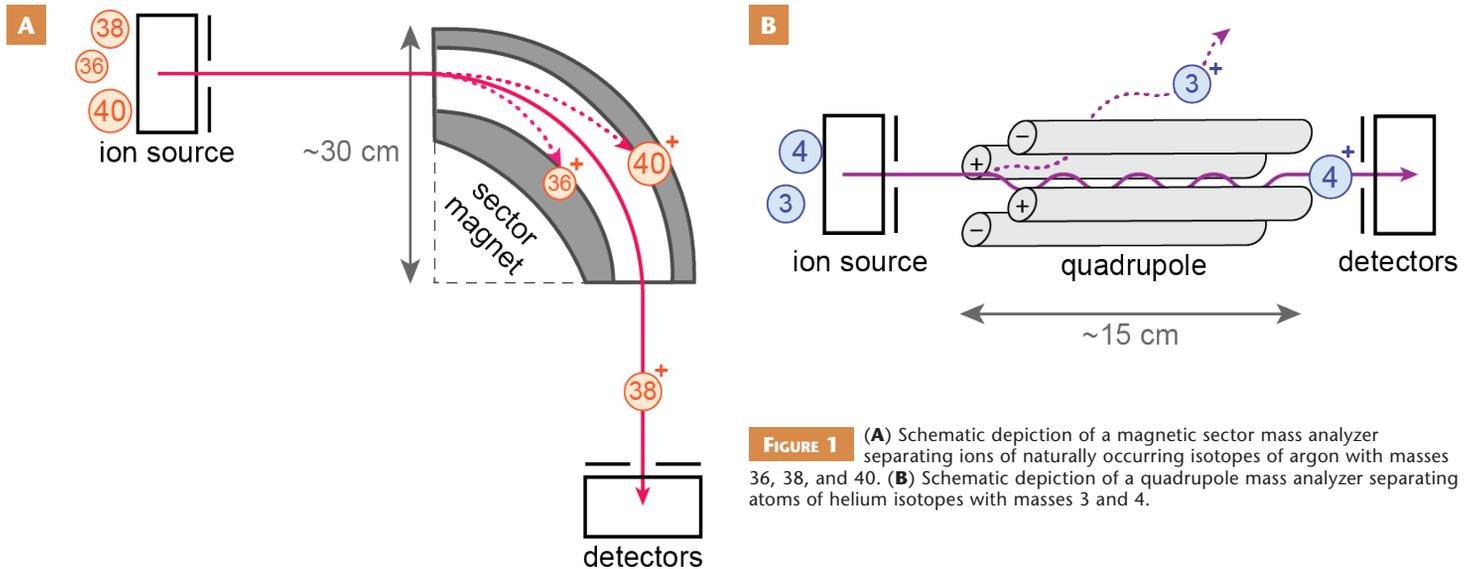


FIGURE 1 (A) Schematic depiction of a magnetic sector mass analyzer separating ions of naturally occurring isotopes of argon with masses 36, 38, and 40. (B) Schematic depiction of a quadrupole mass analyzer separating atoms of helium isotopes with masses 3 and 4.

center to a collector so that one particular ion species is selected at a time; others are directed to collide with the rods (FIG.1B). Different ions can be selected by changing the RF and DC voltages on the rods.

Compared to magnetic sectors, quadrupoles generally operate faster and have a much smaller volume. They are also much less expensive. However, quadrupoles typically have lower mass resolution than magnetic sectors and only allow transmission of one isotope at a time. Because of these differences, magnetic sectors are usually preferred for measurements of low-abundance noble gases and/or where measurement precision is a critically limiting factor. Most measurements for ${}^4\text{He}/{}^3\text{He}$ and ${}^{40}\text{Ar}/{}^{39}\text{Ar}$ thermochronology have been done using a magnetic-sector instrument, whereas ${}^4\text{He}$ abundance measurements for conventional (U–Th)/He analyses by isotope dilution can be carried out with a quadrupole.

Detection

There are two types of detectors typically used for noble gas analyses: Faraday cups, and electron multipliers. Faraday cups place a conductive metal target in a circuit that converts a current to a voltage. The current, caused by ions hitting the detector and generating a small net charge, is measured across a very stable and high-value resistor (typically 10^{11} – 10^{13} Ω) in an amplifier. In electron multipliers, the ion beam impacts a primary metal surface and generates secondary electrons, which are then accelerated across a potential difference into either a series of metal surfaces that have increasing electric potentials or into a continuous curved surface with an increasing electric potential, so generating increasingly larger electron showers as they impact each surface. Faraday cups have stable, linear relationships between ion-beam intensity and measured voltage over a wide range of ion beam intensities, but they have intrinsic noise that makes it difficult to measure small ion beams precisely. Conversely, while electron multipliers lack the stability, linearity, and ion-beam range of Faraday cups, they can be used to measure smaller ion beams because they can have very low intrinsic noise. The recent introduction of capacitive amplifiers and 10^{13} Ω resistors for Faraday systems reduces their electronic noise substantially and increases their sensitivity, such that much smaller ion beams can be measured on Faraday cups, which is a potentially big advantage for noble gas thermochronology. What has also become

quite common is to outfit sector instruments with multicollector arrays laid out to collect multiple beams at once, thereby shortening analysis times and increasing measurement precision.

For ${}^{40}\text{Ar}/{}^{39}\text{Ar}$ thermochronology, this is effectively the end of the measurement process. But for (U–Th)/He and ${}^4\text{He}/{}^3\text{He}$ thermochronology, the buck doesn't stop there. We must also measure the abundance of ${}^4\text{He}$ parent isotopes U and Th (and sometimes Sm), which typically requires wet chemistry followed by measurements with inductively coupled plasma mass spectrometry (ICP-MS).

This Toolkit provides an overview of how we go from noble gas atoms trapped inside a mineral to a measurement that can be used for thermochronology, but our description of this measurement process is by no means exhaustive. In detail, there are a number of phenomena that happen to noble gas atoms during the measurement process—such as mass discrimination and isobaric interference—that we must account for in order to accurately calculate isotope ratios or calibrate abundances from the raw measurements we get at the end of this process. The interested reader should see Burnard et al. (2013) for a more detailed review of these phenomena and how we can account for them.

ACKNOWLEDGMENTS

We thank Ryan Ickert, Sam Boone, and an anonymous reviewer for their feedback.

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