APPLICATION NOTE

Precise argon isotope measurements using SIRIX stable isotope ratio mass spectrometer

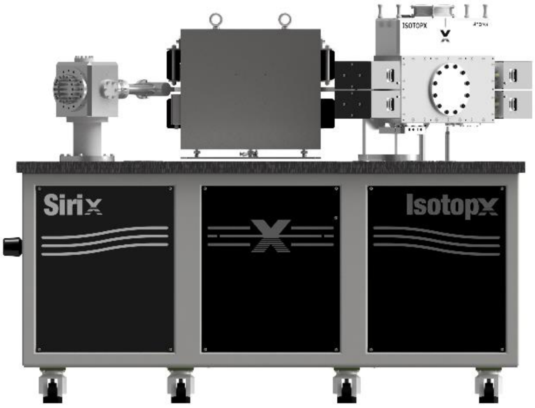
AN25_02 / David Rousell, Matt Hockley, Steve Guilfoyle

Why use IRMS to measure argon isotope ratios?

Introduction

The measurement of argon isotope ratios has been a routine part of geochemistry for many decades. In particular, the argon-argon dating method measures the ratio of 40Ar to 39Ar in order to determine the age of rocks and minerals. But measurement of other isotopes of argon is also scientifically useful. The abundance of 36Ar and 38Ar, along with their ratios to 40Ar, helps scientists understand the composition and origin of the Earth's atmosphere. Furthermore, the amount of these isotopes present in extraterrestrial samples helps us understand the formation and loss of atmospheres in other worlds.

It is common for these isotopes to be measured using a noble gas MS, such as the Isotopx NGX. In these instruments, a sample of gas is injected into the vacuum envelope and the relevant isotope ratio is measured until all of the gas is consumed. No additional gas is injected, hence the name “static vacuum” is often used for this type of mass spectrometer.



A static vacuum instrument is ideal for very small samples such as purified samples from gases trapped in rocks. However, the precision is somewhat limited by the sample size and duration of measurement. What about if you have plenty of sample? Several leading Earth science groups around the world have turned to stable isotope mass spectrometers (often referred to as “IRMS”), most notably Seltzer and Bekaert[1].

Ice cores are a helpful repository of historical temperature information

Using IRMS for argon isotope ratios

However, in order to use an IRMS (a pumped or “dynamic”) mass spectrometer, the sample sizes required are much larger. If you have sufficient sample, for example the gas contained in air bubbles from ice core samples, then there is the potential for significantly higher quality data. A constant pressure can be maintained in the source (reducing fractionation effects), thereby minimizing one of the greatest sources of error.

Even better, a dual inlet sample preparation system can be used. This allows switching between the sample and a known, verified standard at regular intervals. Using the known standard as a reference isotope ratio can improve both precision and accuracy of the analyte isotope ratio.

The problems with using IRMS for argon isotope ratios

Unfortunately there are a number of factors that can make this measurement difficult or can limit the potential gains in precision. The first is that most IRMS instruments are preconfigured for the analysis of certain light isotopes. The Faraday detectors that collect the ion beams may not be moveable, meaning that the analyst has to use a “peak jumping” technique to measure the isotopes in sequential steps. This is less efficient and less precise than full multicollection where all isotopes are measured simultaneously.

A second issue is that the long measurements required by this analysis require a stable mass spectrometer platform to minimize the detector noise, detector drift and other characteristics that can lead to a reduction in data quality. And the mass spectrometer platform ideally needs to have been designed to work in this part of the mass range, not always the case for IRMS instruments.

And finally, the relative size of the 40Ar beam can be an issue when measuring the (much less abundant) 36Ar and 38Ar ion beams. This is due to the peak tailing from the 40Ar interfering with the measurement of the less abundant isotopes. The Selzer paper mentioned above highlights this issue very clearly, showing a 1-2% contribution from the 40Ar when measuring the 38Ar, indicating an abundance sensitivity of around 15-20 ppm (figure 1).

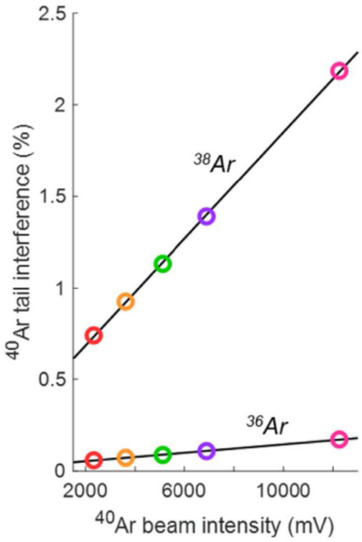


Figure 1: The fractional contribution (in %) to the 36Ar and 38Ar measurements from the 40Ar peak tail, from Selzer et. al.

SIRIX large radius stable isotope ratio mass spectrometer

The SIRIX mass spectrometer design is essentially a Phoenix thermal ionization mass spectrometer, with the thermal ionisation source removed and replaced with a high efficiency electron bombardment gas source.

The SIRIX ion source is constructed of high purity stainless steel. It is pumped with a 300 l/s turbomolecular pump backed with an oil-free scroll pump. Ions are accelerated through a potential of 10 KV, through an exit slit of 0.3 mm width. Ions are focused in the X-Y-Z direction.

The large electromagnet produces a mass dispersion of 610 mm. This was designed for TIMS applications, but is well suited for argon studies as the isotope peaks are well separated at the collector, thereby reducing peak tailing and improving the abundance sensitivity. The base mass resolution of the SIRIX is 600 (10% valley) which is higher than most other gas source instruments. The high resolution ensures that hydrocarbons cannot interfere with peak centers.

All of the SIRIX Faraday collectors are fully adjustable, this means that all of the argon isotopes can be measured simultaneously. No peak jumping is required, improving measurement efficiency and precision. Furthermore, other Faraday collectors can be used for either baseline measurements, background correction of potential interfering species or else direct measurement of the abundance sensitivity, additionally improving the potential precision.

An example of the peak shape and ion beam coincidence is shown in Figure 2. All Faraday collectors have 1mm entrance slits resulting in the same peak widths across the collector. Flat topped peaks are generated because the ion beam width is 0.3 mm.

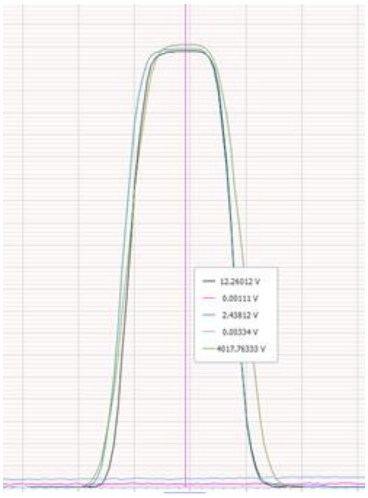


Figure 2. Collectors positioned to have coincidence of 36Ar, 38Ar and 40Ar. Other collectors positioned to monitor baselines, abundance sensitivity and interference peaks.

SIRIX abundance sensitivity

As discussed above, the abundance sensitivity of the mass spectrometer is a key point in obtaining the highest quality data for argon isotope ratio measurements. The design and construction of SIRIX follows the methodology used for TIMS instruments and therefore the abundance sensitivity is excellent; around 2 ppm at m/z 39 relative to 40Ar, and around 0.5 ppm at m/z 38 (38Ar) relative to 40Ar (Figure 3). This is around *twenty five times better* abundance sensitivity than that depicted in Selzer et. al.

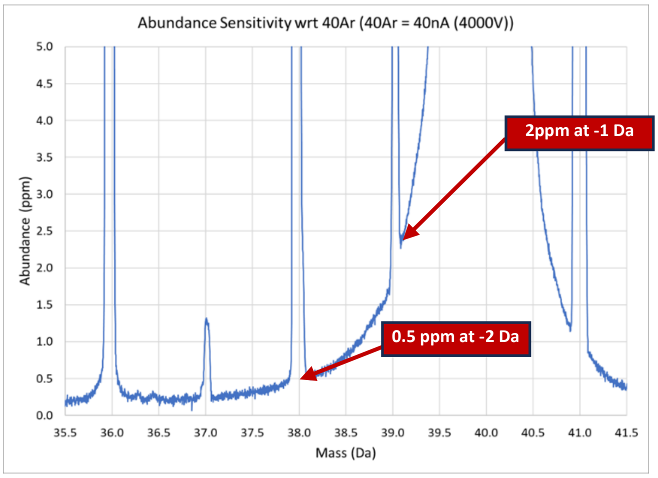


Figure 3. SIRIX abundance sensitivity depicting the contribution from the 40Ar ion beam at lower masses. This equates to an abundance sensitivity of 2 ppm at -1 Da and 0.5 ppm at -2 Da (the latter corresponding to 38Ar)

The benefit of this abundance sensitivity is that the contribution from the 40Ar to the 36Ar and 38Ar measurements is significantly smaller than similar measurements made with other large IRMS instruments. By example, the contribution to the 38Ar isotope from the 40Ar isotope tail will be less than 0.1%, low enough to have a limited effect on the data quality. This is helped by the fact that with SIRIX, a spare Faraday collector can be used to make an *in-situ* measurement of the abundance sensitivity. In similar instruments the contribution from 40Ar at 38Ar may be over 1% and not as readily accounted for.

In addition, there is no evidence of any other baseline artefacts, for example from collisions with the flight tube. This is due to internal baffling and the wide flight tube.

Isotope ratio precision (raw data)

For the best quality, most reproducible data, an IRMS is used in conjunction with a dual inlet. This is a device to automate the sample-standard bracketing system. However, a sterner test of the analytical capabilities of the instrument is to collect *raw* isotope ratio data. This highlights the stability of the mass spectrometric platform – all forms of potential instability such as changes in fractionation, collector noise and instrumental tuning drift will be readily noticeable.

For this test we performed a one hour analysis, consisting of five second integrations per cycle and 60 cycles per block. The peak centre was measured before each block. The raw Ar36/Ar40 and Ar38/Ar40 ratios, as well as the raw Ar40 count rate, are depicted in figure 4. A summary of the block data is shown in table 1.

The sample was simply an argon gas bottle connected by capillary tube to the mass spectrometer. No attempt was made to pressure balance the source, and this can be readily observed in the (linear) reduction in the 40Ar signal over time as the gas sample was consumed. The raw isotope ratios, depicted in the lower two traces, show no drift or trend. Note that this is RAW data, there is no internal correction for mass bias, and no dual inlet to correct for any form of instrumental instability.

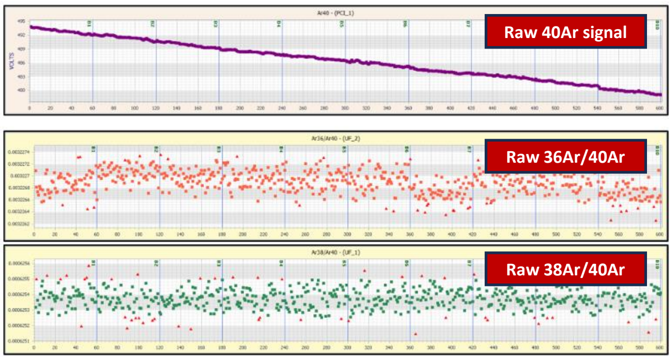


Figure 4. Raw 40Ar signal intensity (upper trace) and raw, uncorrected isotope ratio data for 36Ar/40Ar and 38Ar/40Ar (lower two traces). The 40Ar signal intensity is decaying due to the sample being depleted over time

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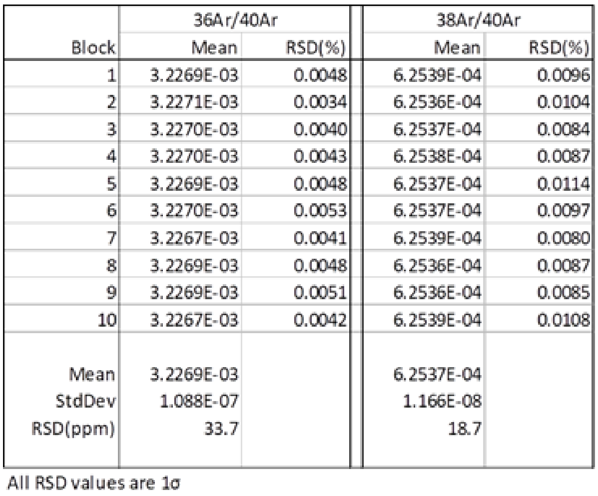

	36Ar/40Ar		38Ar/40Ar	
Block	Mean	RSD(%)	Mean	RSD(%)
1	3.2269E-03	0.0048	6.2539E-04	0.0096
2	3.2271E-03	0.0034	6.2536E-04	0.0104
3	3.2270E-03	0.0040	6.2537E-04	0.0084
4	3.2270E-03	0.0043	6.2538E-04	0.0087
5	3.2269E-03	0.0048	6.2537E-04	0.0114
6	3.2270E-03	0.0053	6.2537E-04	0.0097
7	3.2267E-03	0.0041	6.2539E-04	0.0080
8	3.2269E-03	0.0048	6.2536E-04	0.0087
9	3.2269E-03	0.0051	6.2536E-04	0.0085
10	3.2267E-03	0.0042	6.2539E-04	0.0108
Mean	3.2269E-03		6.2537E-04	
StdDev	1.088E-07		1.166E-08	
RSD(ppm)	33.7		18.7	

All RSD values are 1σ

Table 1. Block data for 10 blocks, each consisting of five second integrations per cycle and 60 cycles per block. The RSD values are 33.7 ppm 1RSD (36Ar/40Ar) and 18.7 ppm 1RSD (38Ar/40Ar).

Improving the isotope ratio precision

As mentioned previously, the addition of a dual inlet device is known to benefit reproducibility and accuracy, particularly over the course of longer measurement periods. In due course we will perform much longer measurement cycles using the dual inlet sample introduction technique to establish how precise and accurate the SIRIX system can be for argon isotope ratios under these conditions.

Summary

SIRIX IRMS can be used for the precise measurement of argon isotope ratios. The flexibility of the SIRIX platform, with fully adjustable detectors, means that collector alignment is excellent and positioning the collectors is straightforward. Additional collectors can be used for baseline noise measurement, abundance sensitivity measurement, or correction of interfering species.

The design, construction and ion optical arrangement of SIRIX is ideal for high precision measurements of argon isotopes. The stability of the platform, including large radius magnet, help to ensure long term data reproducibility.

Initial raw isotope ratio data shows excellent reproducibility, better than 35 ppm 1RSD, for both the 36Ar/40Ar and the 38Ar/40Ar isotope ratios. Additionally, the abundance sensitivity of SIRIX is excellent, with significantly less contribution from the 40Ar ion beam at 36Ar and 38Ar than equivalent instruments from other vendors.

Reference

Alan M. Seltzer, David V. Bekaert. A unified method for measuring noble gas isotope ratios in air, water, and volcanic gases via dynamic mass spectrometry, International Journal of Mass Spectrometry, Volume 478, August 2022, 116873