APPLICATION NOTE

Precise argon isotope measurements using SIRIX stable isotope ratio mass spectrometer

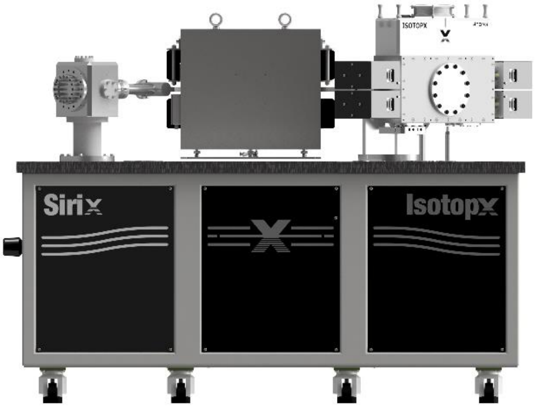
AN25_02 / David Rousell, Matt Hockley, Steve Guilfoyle

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 ^{40}Ar to ^{39}Ar in order to determine the age of rocks and minerals. But measurement of other isotopes of argon is also scientifically useful. The abundance of ^{36}Ar and ^{38}Ar 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 necessitated 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 ^{40}Ar beam can be an issue when measuring the (much less abundant) ^{36}Ar and ^{38}Ar ion beams. This is due to the peak tailing from the ^{40}Ar 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 ^{40}Ar when measuring the ^{38}Ar, indicating an abundance sensitivity of around 15-20 ppm (figure 1).

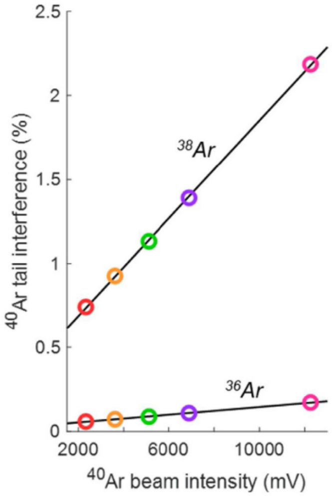


Figure 1: The fractional contribution (in %) to the ^{36}Ar and ^{38}Ar measurements from the ^{40}Ar peak tail, from Selzer et. al.

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.

In addition, all of the SIRIX Faraday detectors use a high dynamic range, low noise amplifier system. There is no need to select the appropriate amplifier gain; an additional complexity required for other IRMS instruments when used for this application.

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.

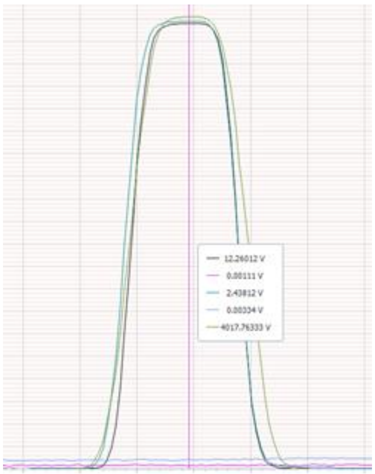


Figure 2. Collectors positioned to have coincidence of ^{36}Ar, ^{38}Ar and ^{40}Ar. Other collectors positioned to monitor baselines, abundance sensitivity and interference peaks.

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 ^{40}Ar, and around 0.5 ppm at m/z 38 (^{38}Ar) relative to ^{40}Ar (Figure 3). This is around *twenty five times better* abundance sensitivity than that depicted in Selzer et. al.

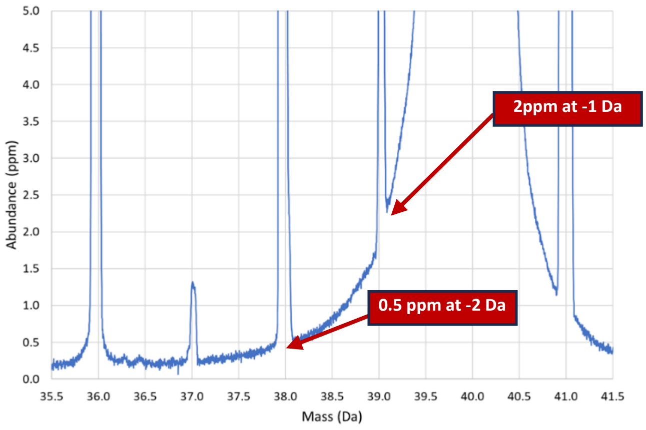


Figure 3. SIRIX abundance sensitivity depicting the contribution from the ^{40}Ar ion beam at lower masses. This equates to an abundance sensitivity of 2 ppm at -1 Da and 0.5 ppm at -2 Da (the latter corresponding to ^{38}Ar)

The benefit of this abundance sensitivity is that the contribution from the ^{40}Ar to the ^{36}Ar and ^{38}Ar measurements is significantly smaller than similar measurements made with other large IRMS instruments. By example, the contribution to the ^{38}Ar isotope from the ^{40}Ar 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 ^{40}Ar at ^{38}Ar 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.

In this study, the sample was argon gas from a reservoir 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 ^{40}Ar signal over time as the gas sample was consumed. For this test we performed a single analysis containing 10 blocks where the ^{40}Ar signal was ~450V (~4.5nA). Each block consisted of 60 cycles; the integration time of each cycle was 5s. The analysis time was approximately 5.5 minutes per block. Peak centring was performed at the start of each block.

The raw ^{40}Ar/^{36}Ar and ^{38}Ar/^{36}Ar ratios, as well as the raw ^{40}Ar count rate, are depicted in figure 4. 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. This raw, uncorrected data produced external reproducibilities (^{40}Ar/^{36}Ar and ^{38}Ar/^{36}Ar) of 25-50 ppm 1σ. These are exceptional values for raw, uncorrected isotope ratios with no dual inlet utilised.

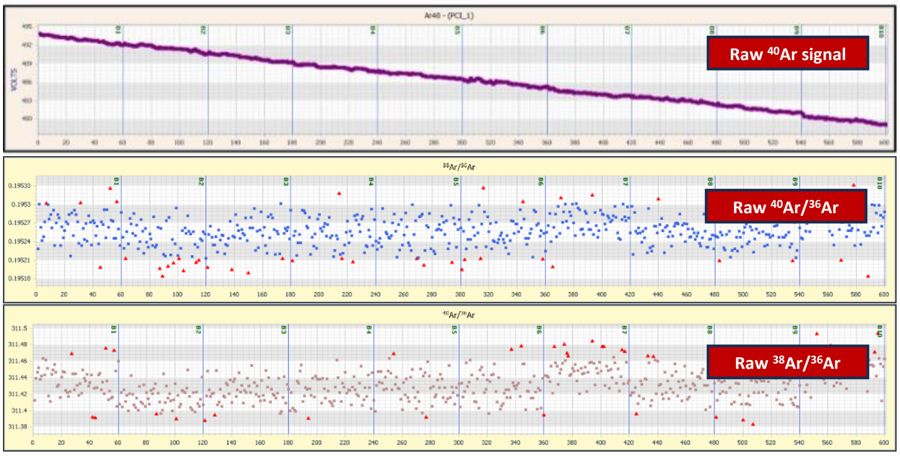


Figure 4. Raw ^{40}Ar signal intensity (upper trace) and raw, uncorrected isotope ratio data for ^{40}Ar/^{36}Ar and ^{38}Ar/^{36}Ar (lower two traces). The ^{40}Ar signal intensity is decaying due to the sample being depleted over time

APPLICATION NOTE

Precise argon isotope measurements using SIRIX stable isotope ratio mass spectrometer

AN25_02 / David Rousell, Matt Hockley, Steve Guilfoyle

	$^{40}Ar/^{36}Ar$		$^{38}Ar/^{36}Ar$	
Block	**Mean**	**StErr 2σ (ppm)**	**Mean**	**StErr 2σ (ppm)**
1	323.0000	7	0.197997	17
2	323.0026	8	0.198003	12
3	322.9984	7	0.198002	18
4	323.0014	7	0.198001	16
5	323.0016	8	0.197999	14
6	323.0004	7	0.198000	17
7	322.9958	6	0.197999	17
8	323.0014	8	0.198001	15
9	322.9976	6	0.197996	15
10	323.0009	6	0.198003	22
Mean	**323.0000**		**0.198000**	
StDev	**0.0021**		**0.000002**	
1RSD ppm	**6.54**		**11.54**	

Table 1. Block data for 10 blocks, each consisting of five second integrations per cycle and 60 cycles per block. The RSD values are 6 ppm 1RSD ($^{40}Ar/^{36}Ar$) and 11 ppm 1RSD ($^{38}Ar/^{36}Ar$).

Improving the isotope ratio precision

To emulate dual inlet data, a second set of data was acquired. In this dataset, odd numbered cycles from this dataset were regarded as reference gas and even cycles were regarded as sample gas. Reference measurements either side of the sample measurements, X-1 and X+1, were averaged to calculate each sample data point. For each block, sample ratios outside ±2σ were rejected and the average calculated.

This data is summarised in table 1. The external reproducibility values are 6 ppm 1σ for the $^{40}Ar/^{36}Ar$ ratio and 11 ppm 1σ for the $^{38}Ar/^{36}Ar$ ratio. This is comparable to the best currently published data (Selzer et. al.). In a forthcoming experiment, the SIRIX will be connected to a dual inlet in order to fully establish the capabilities of this instrument.

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. Furthermore, no selection of Faraday amplifier gain is required, as all of the SIRIX Faraday detectors use ATONA amplifiers with huge dynamic range and extremely low noise levels.

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, helps to ensure long term data reproducibility.

Initial *raw* isotope ratio data shows excellent reproducibility, better than 50 ppm 1σ for both the $^{40}Ar/^{36}Ar$ and the $^{38}Ar/^{36}Ar$ isotope ratios. By emulating dual inlet analysis, reproducibilities of 6 ppm 1σ for the $^{40}Ar/^{36}Ar$ ratio and 11 ppm 1σ for the $^{38}Ar/^{36}Ar$ ratio were achieved.

Additionally, the abundance sensitivity of SIRIX is excellent, with significantly less contribution from the ^{40}Ar ion beam at ^{36}Ar and ^{38}Ar 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