

Measurement of $^{87}\text{Sr}/^{86}\text{Sr}$ Isotope Ratios in Rocks by ICP-QQQ in Mass-Shift Mode

The direct Agilent 8900 ICP-QQQ method removes need for chromatographic separation of ^{87}Sr and ^{87}Rb



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Introduction

Triple quadrupole ICP-MS (ICP-QQQ) instrumentation is increasingly used for isotope ratio (IR) analysis studies (1–5). Geologists use radioactive isotopes that have long half-lives to date rocks and sediments, often with the choice of dating method dependent on the type of samples under investigation. For example, rubidium (Rb) is abundant in many potassium-containing rocks, so the Rb-strontium (Sr) β -decay scheme is used in geochronology studies of igneous, and sometimes metamorphic rocks and minerals (5, 6).

Strontium (Sr) has four naturally occurring isotopes: ^{84}Sr (0.56% abundance), ^{86}Sr (9.86% abundance), ^{87}Sr (7.00% abundance), and ^{88}Sr (82.58% abundance). While these are the four stable isotopes of Sr, the abundance of ^{87}Sr varies over long periods of time due to the formation of radiogenic ^{87}Sr following β -decay of ^{87}Rb .

The level of ^{87}Sr compared to ^{86}Sr is dependent on the original concentration of Rb in the environmental or geological system. Therefore, $^{87}\text{Sr}/^{86}\text{Sr}$ IR measurements can also serve as a tracer of ecosystem processes (7).

Traditional IR measurement techniques such as thermal ionization mass spectrometry (TIMS) or multicollector inductively coupled plasma mass spectrometry (MC-ICP-MS) offer excellent accuracy and high precision for most IR studies. However, they are less efficient for the measurement of β decay product isotopes, due to isobaric interferences of the daughter isotope by their respective parent isotope. For example, ^{87}Sr must be separated from ^{87}Rb before analysis by TIMS or MC-ICP-MS to avoid the isobaric spectral overlap at mass 87. This process is labor-intensive and time consuming, especially for large sample numbers that are typical of geological and environmental survey studies. By contrast, no Rb/Sr separation is needed before analysis using ICP-MS/MS methodology, simplifying the analysis and improving sample throughput. ICP-MS/MS methods use "chemical resolution" to resolve isobaric interferences, as demonstrated in previous studies using Agilent ICP-QQQ instrumentation (1, 5).

In those studies, reactive gases were used in the collision/reaction cell (CRC) of the ICP-QQQ to separate the isobaric overlap from ^{87}Rb on ^{87}Sr , avoiding the need for chromatographic separation. Isobaric ion interferences can be separated using ICP-QQQ when the cell gas reacts quickly with one of the elements to form a product ion, while the other element does not react (or reacts slowly). Although reaction cell gases such as CH_3F , N_2O , and SF_6 provide a higher reaction rate with Sr^+ than O_2 , O_2 is more widely available in laboratories and is more suited to routine applications.

The aim of this study was to develop a fast, high throughput, routine method suitable for the accurate determination of $^{87}\text{Sr}/^{86}\text{Sr}$ IR with precision below 0.1% RSD. To achieve the objective, an Agilent 8900 ICP-QQQ was operated in MS/MS mass-shift mode using O_2 as the cell gas.

$^{87}\text{Sr}/^{86}\text{Sr}$ IR analysis by ICP-QQQ in O_2 mass-shift mode

The Agilent 8900 Triple Quadrupole ICP-MS (ICP-QQQ) uses two identical, full-sized quadrupoles (Q1 and Q2), one before and one after the ORS⁴ reaction cell. Like the analyzer mass filter, Q2, Q1 operates in a high vacuum region, so it provides excellent resolution and abundance sensitivity. This allows precise selection of which ions enter the cell, ensuring the reactions used to resolve the analyte ions from their on-mass interferences are consistent and predictable. As shown in

Figure 1, by setting Q1 to m/z 87, only Rb-87 and Sr-87 enter the cell that is pressurized with O_2 . In the cell, $^{87}\text{Sr}^+$ reacts with O_2 to form $^{87}\text{Sr}^{16}\text{O}^+$ product ion, while $^{87}\text{Rb}^+$ does not react. The second quadrupole (Q2) is set to $m/z=103$, which allows $^{87}\text{Sr}^{16}\text{O}^+$ to pass to the detector, free of interference.

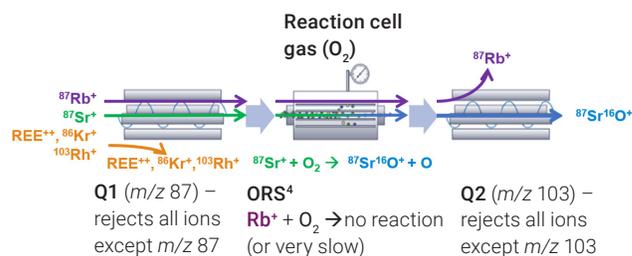


Figure 1. Determination of ^{87}Sr as $^{87}\text{Sr}^{16}\text{O}^+$ product ion using ICP-QQQ operating in mass-shift mode with O_2 cell gas.

Efficiency of using mass-shift mode to separate Sr from Rb

When Sr^+ ions react with O_2 in the cell, not all Sr^+ ions complete the reaction to form SrO^+ ions during the short transit time in the cell. To optimize the O_2 flow rate, counts per second (cps) of both $^{86}\text{Sr}^+$ (at m/z 86) and $^{86}\text{Sr}^{16}\text{O}^+$ (at m/z 102) were monitored. For the calculation, the measured cps of Q1 ($m/z = 86$) \rightarrow Q2 ($m/z = 102$) was divided by the cps of Q1 ($m/z = 86$) \rightarrow Q2 ($m/z = 86$). The mass-shift efficiency of Sr in O_2 reaction mode ranged between the expected range of 10 and 14% (8). The variation was mainly due to instrument conditions on the day of measurement.

To evaluate whether $^{87}\text{Rb}^{16}\text{O}^+$ formed in the cell sufficiently to affect the measurement of $^{87}\text{Sr}^{16}\text{O}^+$, ^{85}Rb was used as a proxy for ^{87}Rb . The signals at m/z 85 (for $^{85}\text{Rb}^+$) and m/z 101 (for $^{85}\text{Rb}^{16}\text{O}^+$) were monitored during method development. First, Q1 and Q2 were both set to $m/z = 85$. The measured cps of $^{85}\text{Rb}^+$ in the reference materials (RMs) and rock samples were between 6×10^5 and 4×10^6 (the cps of $^{85}\text{Rb}^+$ in the solution blank was typically below 1). Then Q2 was set to m/z 101 and the measured cps range was below 1, suggesting minimal formation of $^{85}\text{Rb}^{16}\text{O}^+$ in the cell. Using the natural abundance of ^{85}Rb (72.17%) and ^{87}Rb (27.83%), we calculated that the conversion of $^{87}\text{Rb}^+$ to $^{87}\text{Rb}^{16}\text{O}^+$ would lead to a measured cps for $^{87}\text{Rb}^{16}\text{O}^+$ at $m/z = 103$ below 0.4 cps.

In this study, the Sr concentration of the RMs and rock samples measured by ICP-QQQ were mostly around 100 ng/mL. This concentration is equivalent to over 1×10^5 cps for $^{87}\text{Sr}^+$ as $^{87}\text{Sr}^{16}\text{O}^+$ ($m/z = 103$). Therefore, the interference effect of $^{87}\text{Rb}^{16}\text{O}^+$ ($m/z = 103$) on $^{87}\text{Sr}^{16}\text{O}^+$ ($m/z = 103$) is negligible in this study.

Experimental

Standards and sample preparation

To determine the accuracy and precision of the method, three US Geological Survey (USGS) RMs were used: Basalt, Columbia River (BCR-2), Basalt, Hawaiian Volcanic Observatory (BHVO-2), and Andesite (AGV-2). Twenty-three rock samples were analyzed in the study, including basalt (Rb/Sr concentration ratio 0.02–0.12), dolerite (Rb/Sr concentration ratio 0.04–0.10), andesite (Rb/Sr concentration ratio 0.76–0.87), and rhyolite (Rb/Sr concentration ratio 5.6–9.1).

All RMs and samples were prepared at the Institute of Tibetan Plateau Research, Chinese Academy of Sciences (ITP-CAS) using a classic pressurized acid digestion method for trace element measurements. Approximately 50 mg of each sample was digested using 1 mL each of purified HNO₃ and HF in a closed vessel oven, heated at 190 °C for 36 hours. Following the addition of 0.25 mL of HClO₄, the sample was evaporated to incipient dryness on a hot plate at 130 °C. This procedure was repeated with the addition of 0.5 mL of HNO₃. The sample was further heated at 170 °C until white fumes were seen. 0.5 mL of 40% HNO₃ was added, and the sample was oven-heated at 130 °C for 3 h. After cooling, 49.5 mL of de-ionized water was added to the sample, ready for analysis by ICP-QQQ.

Instrumentation

An Agilent 8900 ICP-QQQ was used. The sample introduction system consisted of a quartz torch with 2.5 mm i.d. injector, a quartz spray chamber, glass concentric nebulizer, and nickel-tipped interface cones. Samples were introduced into the ICP-QQQ using a standard peristaltic pump and Agilent SPS 4 autosampler.

⁸⁷Sr and ⁸⁶Sr were determined in mass-shift mode using O₂ as the cell gas. The isobaric interference on ⁸⁷Sr by ⁸⁷Rb was avoided by measuring the Sr product ions ⁸⁷Sr¹⁶O⁺ and ⁸⁶Sr¹⁶O⁺ at *m/z*=103 and *m/z*=102, respectively. Typical instrument operating parameters are listed in Table 1.

Throughout the analytical workflow, a BCR-2 RM sample solution containing 100 ng/mL Sr was measured after every two or three samples to ensure that the mass bias calibration was up to date. Instrument mass bias occurs when ions of different element masses transmit through the ICP-MS with different efficiencies, resulting in inaccurate IR measurements. The Agilent ICP-MS MassHunter software automatically updates the mass bias.

Table 1. ICP-QQQ operating parameters and acquisition settings for ⁸⁷Sr/⁸⁶Sr IR analysis.

Parameter	Setting
RF Power (W)	1550
Sampling Depth (mm)	8.0
Nebulizer Gas Flow Rate (L/min)	1.15
KED (V)	-6.0
Cell Gas Flow Rate (mL/min)	0.45 (30% of full scale)
Axial Acceleration (V)	1.0
Q1→Q2 Masses (<i>m/z</i>)	86→ 102 87→ 103
Q2 Peak Pattern	1 point
Replicates	7
Sweeps	1000
Integration Time of Each Mass (s)	9

Results and discussion

Determination of ⁸⁷Sr/⁸⁶Sr IRs in the RMs

⁸⁷Sr/⁸⁶Sr IRs were measured in BCR-2 and BHVO-2 RMs using the ICP-QQQ mass-shift method with O₂ cell gas. To confirm that chromatographic separation of Sr wasn't needed for successful ICP-QQQ analysis, data was acquired with and without the Sr purification stage. Each RM was measured seven times in different batches or on different days, with seven replicate measurements.

The ⁸⁷Sr/⁸⁶Sr ratio results in Figure 2 show that there was no significant difference in the results for BCR-2 and BHVO-2 with and without Sr purification. Both sets of measured data are within the literature reported values that were obtained using TIMS and MC-ICP-MS (9). The ICP-QQQ method is accurate enough to study ⁸⁷Sr/⁸⁶Sr ratios in natural samples/systems with a wide range of ⁸⁷Sr/⁸⁶Sr distributions. Also, the sample preparation procedure doesn't affect the precision of the ICP-QQQ measurements.

The error bars show two times the standard deviation (SD) of the average of seven separate measurements of the two RMs, which range between 0.0003 and 0.0005 (n=7) or between 0.02 and 0.04% RSD. This deviation is significantly higher than the RSD of the MC-ICP-MS method. However, the results show that ICP-QQQ can distinguish ⁸⁷Sr/⁸⁶Sr ratios of materials within 0.001 (i.e. 0.1%) precision.

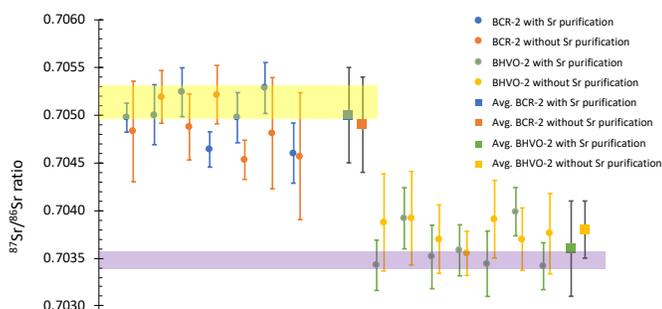


Figure 2. Comparison of the measured $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of BCR-2 and BHVO-2 with and without Sr purification column chemistry by ICP-QQQ with literature values (9) represented by the shaded bands. Circle symbols: average value of each measurement, the error bar is 1SD of the seven replicates of each measurement. Square symbols: the average value of the seven measurements of BCR-2 and BHVO-2, the error bar represents 2SD of the seven measurements.

The effect of the Sr concentration in the samples

To optimize the level of sample dilution of the sample digests, we investigated the effects of the concentration of Sr in the rock samples on the analysis. Three fully digested rock samples (andesite, dolerite, and basalt) were diluted to give a Sr concentration between 60 and 350 ng/mL. A BCR-2 solution containing 100 ng/mL of Sr was used for online instrumental mass bias correction.

The results in Table 2 show that, within the measured concentration range, the Sr concentration doesn't significantly affect the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of each type of sample. Therefore, the digested samples could potentially be diluted into a certain range, such as from 60 to 350 ng/mL, according to a standard operation procedure, simplifying the analysis.

Table 2. Measured $^{87}\text{Sr}/^{86}\text{Sr}$ IRs of three different rock samples (one sample of each type of rock) with four different Sr concentrations.

Sample	Sr Concentration (ng/mL)	$^{87}\text{Sr}/^{86}\text{Sr}$ Ratio	2SD (n=3)
Basalt	70	0.7036	0.0009
	100	0.7055	0.0002
	175	0.7043	0.0008
	350	0.7060	0.0009
Dolerite	70	0.7035	0.0015
	100	0.7047	0.0009
	170	0.7039	0.0016
	340	0.7046	0.0008
Andesite	60	0.7114	0.0013
	100	0.7126	0.0006
	140	0.7120	0.0015
	280	0.7126	0.0014

Analysis of Sr IRs of rock samples by ICP-QQQ

The 23 rock samples were analyzed in triplicate (n=3) using the ICP-QQQ mass-shift method, without Sr purification. As shown in Figure 3, the samples cover a large $^{87}\text{Sr}/^{86}\text{Sr}$ ratio range from 0.705 to 0.748. This range is typical of common rocks (Figure 3), as well as minerals, waters, and plants (4).

The accuracy of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio measurements obtained by ICP-QQQ was compared with data obtained by MC-ICP-MS. There was good agreement between the two methods (4), with a variation of between 0.00001 and 0.0016 of the mean of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio. The variation wasn't dependent on the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio range.

The precision of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio measured by ICP-QQQ varied between 0.0001 and 0.0019 (2SD, n=3) or between 0.01 and 0.13% (RSD, n=3). While this precision is lower than the precision of the MC-ICP-MS method, it is sufficient for applications with large $^{87}\text{Sr}/^{86}\text{Sr}$ ratio differences, such as the identification of $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in between certain rock types. Andesite, rhyolite, and dolerite rock samples have significant $^{87}\text{Sr}/^{86}\text{Sr}$ ratio variations, as shown in Figure 3. However, distinguishing rock types within a narrow range of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, e.g., low $^{87}\text{Sr}/^{86}\text{Sr}$ basalts, could be challenging.

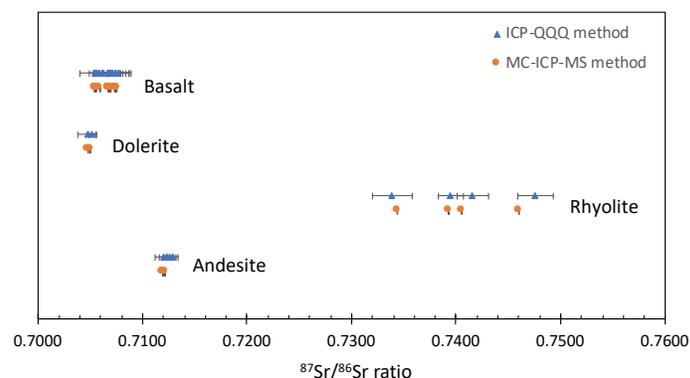


Figure 3. $^{87}\text{Sr}/^{86}\text{Sr}$ IR distribution for typical rocks. Triangle symbol: $^{87}\text{Sr}/^{86}\text{Sr}$ IR of ICP-QQQ method, error bar in 2SD (n=3). Circle symbol: $^{87}\text{Sr}/^{86}\text{Sr}$ IR of MC-ICP-MS method, error bar in 2SD (n=3) which falls within the circle mark.

Conclusion

The study has shown that the Agilent 8900 ICP-QQQ can be used for the accurate measurement of $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios in a range of rock samples. The isobaric interference of ^{87}Rb on ^{87}Sr was resolved using a mass-shift method with O_2 cell gas. Because Sr reacts with oxygen at a much faster rate than Rb, ^{87}Sr was measured as $^{87}\text{Sr}^{16}\text{O}^+$, free from interference from ^{87}Rb . This method is simpler, faster, and less costly than TIMS or MC-ICP-MS methods, as both TIMS and MC-ICP-MS require chromatographic separation of Sr from Rb before analysis. The ICP-QQQ mass-shift method is also suited to nonspecialist laboratories that aren't equipped with TIMS or MC-ICP-MS.

The distribution of $^{87}\text{Sr}/^{86}\text{Sr}$ IRs of natural samples is generally between 0.70 and 0.77, although it can range from 0.700 to 0.943 (4). The accuracy and precision of the ICP-MS/MS method is sufficient to differentiate between various sources when the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio varies by more than 0.001. Therefore, this method has the potential to be used in applications that require source identification, such as environmental pollutant source tracing, large-scale geological surveys, and agricultural product authenticity studies.

More information

For detailed information, please see Liu, X, Dong, S, Yue, Y, et al. $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios in rocks determined by ICP-MS/MS in O_2 mode without prior Sr purification. *Rapid Commun Mass Spectrom.* 2020, <https://doi.org/10.1002/rcm.8690>

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