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Lead Isotope Ratio Optimization using Q-ICP-MS for Volcanic Rocks

Mutiara Effendi [1,*], Indah Yuni Prasetiawati [1], Melnawati Rohman [1]

[1] Center for Geological Survey, Geological Agency, Ministry of Energy and Mineral Resources, Bandung, Indonesia

* Corresponding author: mutiara.effendi@esdm.go.id

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Abstract

Lead isotope ratios are a valuable tool for tracing the origin and evolution of volcanic rocks, supporting exploration of critical metals for renewable energy. While multi-collector and thermal ionization mass spectrometers offer superior precision, they are costly and time-consuming. For rapid, preliminary analyses of lead-rich samples, quadrupole mass spectrometry can provide sufficient results with appropriate optimization. This study aims to optimize the measurement of lead isotope ratios using quadrupole ICP-MS (Q-ICP-MS) for several volcanic rocks from Indonesia. After multivariate optimization of the main operating conditions (dwell time 1-3 ms, sweep number 2000-4000, and replicate 2-6), the isotopic ratios were measured with an internal precision of 0.05-0.9 %RSD; the accuracy is 99.97-103.79 %, and reproducibility is 8.8-10.5 Horwitz value. Our measurements agree well with the reported data of certified reference material AGV-2 and within analytical uncertainties.

1. Introduction

Radiogenic isotopes are essential tools in Earth sciences, acting as natural clocks to date rock formation, geological processes, and mineralization events [1]. However, isotopic abundances of certain elements are not constant, particularly those involved in geochemical processes; thus, more robust isotope ratio measurements are needed.

The lead isotope composition found in geological materials is the combination of the original lead at the time of its formation and the additional radiogenic lead produced over time from the radioactive decay of uranium and thorium. Lead has four stable isotopes, where ^{206}Pb, ^{207}Pb, and ^{208}Pb are radiogenic and derived from the decay of uranium and thorium over geologic time, while ^{204}Pb is non-radiogenic and represents the primordial composition [2]. The concentrations of these radiogenic lead isotopes are typically expressed relative to ^{204}Pb, a stable, non-radiogenic isotope, to enable meaningful comparisons.

Lead isotope ratio is not affected by chemical processes during magma generation, hence it serves as a reliable tracer of the geological history of volcanic regions and is useful for planning better volcanic hazard mitigation in natural disaster management [3]. In terms of mineral exploration and renewable energy development, lead isotope ratios can be used to locate the lead-bearing minerals (galena) useful for industrial applications, precious metals (gold, silver), strategic minerals (Co, Cu, Cr), and critical minerals (Li, REE) [4].

Quadrupole ICP-MS (Q-ICP-MS) offers a practical balance of speed, cost, and acceptable precision, making it suitable for routine or preliminary isotopic analysis [5]. Unlike single-pole ICP-MS, Q-ICP-MS provides better mass resolution and lower background noise. TIMS (Thermal Ionization Mass Spectrometry) remains the gold standard for lead isotope ratio precision due to its ionization efficiency and stability, though it is time-consuming and less ideal for high-throughput analysis. MC-ICP-MS (Multi-Collector ICP-MS) achieves precision close to TIMS with faster analysis and better matrix handling, but at higher operational costs than Q- ICP-MS. Overall, while TIMS and MC-ICP-MS are favored for high-precision applications, Q-ICP-MS is preferred for rapid, cost-effective analysis where moderate precision is acceptable. A detailed comparison is presented in Table 1.

Table 1. Comparative table of lead isotope analysis techniques (summarized from Becker [6] and Gerald [7])

Features	Single-pole ICP-MS	Q-ICP-MS	MC-ICP-MS	TIMS
Precision	Low (≤ 1%)	Moderate (0.1–1% RSD)	Very high (≤ 0.01% RSD)	Very high (≤ 0.001% RSD)
Accuracy	Low	Moderate	Very high	Very high
Mass resolution	Low	Moderate	High	High
Complexity	Low	Moderate	High	High
Sample throughput	High	High	Moderate	Low
Speed	Fast	Fast	Moderate	Slow
Cost	Low	Moderate	High	High
Application	Routine elemental analysis	Routine isotope screening, preliminary isotope study	High precision isotope analysis, provenance studies	High precision geochronology/isotope dating

However, maximizing the analytical performance of Q-ICP-MS requires careful optimization of instrumental parameters. Factors such as mass bias, isobaric interferences, and matrix effects can compromise the precision and accuracy of isotope ratio measurements [8]. Various studies reported that tuning aspects such as dwell time, scan number, signal intensity, and mass scanning rate can significantly enhance precision and reduce noise [9, 10, 11, 12, 13]. Additionally, adjusting the sample uptake rate, spray chamber conditions, and quadrupole voltage has produced highly reproducible results, comparable to more advanced instruments [14, 15, 16].

Despite these improvements, many optimization efforts have been limited to specific sample types or standard materials. There remains a gap in understanding how different geological matrices affect isotopic measurement outcomes. Given the chemical and physical heterogeneity of volcanic rocks, matrix-specific optimization is essential to ensure data quality and analytical robustness.

This study aims to address that need by evaluating and optimizing Q-ICP-MS parameters for lead isotope analysis across six volcanic rock types from Indonesia. Multivariate analysis is increasingly favored in calibration strategies for its effectiveness in correcting matrix effects and handling complex datasets. It provides a more comprehensive and statistically robust interpretation than univariate methods [17].

By exploring how variations in acquisition parameters affect analytical performance for each matrix, this work contributes to the refinement of lead isotope methodologies in geological materials. The findings are expected to support more efficient exploration of critical metals and minerals, which are essential for the advancement of renewable energy technologies.

2. Experimental

2.1. Chemicals and Standards

Experiments were carried out using pure and analytical grade chemicals, as required. All of the solutions were purchased from Merck and used as received. Strong acids were used to dissolve the volcanic samples, in respective order: HNO_3 ultrapure 60% (6 mL), HF pro analysis 40% (6 mL), and $HClO_4$ pro analysis 60% (4 mL). Lead standard series solutions were made from 1 to 50 ppm and measured in line with samples for calibration curves. The analysis was verified with certified reference material AGV-2 from the United States Geological Survey, which was analyzed together with the samples [18].

2.2. Sample Collection and Digestion

Six different matrices of volcanic rocks were collected during fieldwork on Sumatra Island, Indonesia. Rhyolite, scoria, pumice, dacite, and ignimbrite were taken from heavily vegetated Mt. Masurai, Merangin Regency, Jambi, whereas granite was taken from Bangka Island.

Each sample was prepared according to standard procedures commonly used for geological materials, as described by Becker [6]. Rock samples were crushed using a jaw crusher, weighed to 0.1 gram, and digested with strong acids. The mixture was heated on a hotplate below 200°C until nearly dry, then diluted with 5 mL of 60% ultrapure HNO_3 and reheated until the solution became clear. The resulting solution was transferred to a 50 mL volumetric flask and diluted to volume with ultrapure water. A 1 mL aliquot was taken, spiked with Be and Bi as internal standards, and further diluted with 2% HNO_3 to a final volume of 10 mL, ready for analysis.

Table 2. Instrumental characteristics and parameters for lead isotope analysis with Q-ICP-MS

Sector	Specification
Instrument	Thermo Fisher Scientific ICP-MS iCAPQ series
Power and voltage	3750 VA (effective: 3500 W), 230 V
Laboratory temperature	22°C (instrument requirement: 15°C–35°C)
Sample introduction system	Cetac Autosampler ASX-560
Nebulizer (material, flow rate)	PFA, 1.03 L/min
Auxiliary flow rate	0.8 L/min
Spray chamber	Quartz, equipped with a Peltier cooler
Injector	Quartz, 2.5 mm internal diameter
Sample uptake rate and wash rate	30-300 µL/min
Torch	1548 W
Cooling system (type, T, P, supply rate)	Distilled water, 15 to 25°C (optimum at 21°C), 2.5-5.5 bar, > 5.5 L/min
Chiller	NESLAB ThermoFlex 2500 with closed circuit, cooled by a refrigerating device
Interface	Ni/Cu sample cone, Ni skimmer cone, and extraction lens; Temperature 35°C
Mass analyzer	Quadrupole
Detector	Dual-mode secondary electron multiplier (SEM)
Vacuum system	Three-stage pumping system, realized by a rotary pump and split-flow turbo-molecular pump for intermediate and high-stage
Pressure measurement	Active Pirani Gauge (APG) and Active Inverted Magnetron Gauge (AIM)
Plasma and gas supply	Argon (99.99%, max. 24 L/min supply rate, 6 bar) and Helium (99.99%, max. 10 mL/min supply rate, 1 bar)

2.3. Instrumentation and Operating Conditions

The lead isotope ratio analysis was conducted with Q-ICP-MS from Thermo Fisher iCap-Q series. The system was vacuumed throughout the analysis, and the temperature was maintained cold with a chiller. The instrument system was rinsed with 2% HNO_3 for 15 minutes before analysis to minimize the matrix interferences. The detailed instrumental conditions are reported in Table 2.

The optimization of ion formation in the plasma and the mass spectrometer was done with the flow of TUNE B solution to the system, which consists of 1.0 µg/L of Ba, Bi, Ce, Co, In, Li, and U in the solution of 2% HNO_3 and 0.5% HCl. The following isotope intensity waited to stabilize: ^{7}Li > 50,000 cps; ^{39}Co > 100,000 cps, ^{115}In > 220,000 cps, and ^{238}U > 300,000 cps to minimize spectral interferences. Finally, an Autotune procedure was performed to ensure the system was ready for operation.

The experiment design was combined with previous studies [10, 13, 14, 16, 19, 20]. The variations were made on acquisition parameters such as dwell time (1-3 ms), sweep number (2000-4000), and replicates (2-6×). Polyatomic interferences were minimized using collision cell mode (CCT) analysis [21]. Furthermore, isobaric interferences from ^{200}Hg and ^{204}Hg were reduced with a built-in mathematical correction from the operational software [22] according to Equations 1 and 2.

$$^{204}Pb = -0.296152 \times {}^{200}Hg \tag{1}$$

$$^{204}Pb = {}^{204}Ion\ total - {}^{202}Hg \tag{2}$$

2.4. Data Processing

The data were recorded using Qtegra ISDS software in an eQuant quantification mode on the instrument. The validity of the measurement was determined through analytical criteria, such as precision (% RSD < 1), accuracy (~100 % towards CRM value), and reproducibility, as listed in the guidance by the Association of Official Analytical Collaboration International (AOAC) [23].

3. Results and Discussion

The lead isotope composition of various volcanic rocks from Jambi and Bangka Island of Sumatra, Indonesia, is summarized in Table 3. Overall, each matrix yielded different optimum conditions. The calculation of % recovery for CRM AGV-2 was made by Equations 3 and 4 for each ratio of ^{206}Pb/^{204}Pb, ^{207}Pb/^{204}Pb, and ^{208}Pb/^{204}Pb, and the summary is shown in Table 3. The observed values of lead isotopes were divided by the correction factor to get the actual value, and the result is shown in Table 4. Reproducibility is calculated with the Horwitz factor ($PRSD_{(R)}$) using Equation 5, where C is the mass fraction, and the summary is shown in Table 5.

$$Correction\ factor = \frac{Concentration_{observed}}{Concentration_{certificate}} \tag{3}$$

$$Recovery = Correction\ factor \times 100\% \tag{4}$$

$$PRSD(R) = 2C - 0.15 \tag{5}$$

Table 3. Optimum conditions and %RSD for lead isotope measurements for the studied rocks

Sample	Dwell time (ms)	Sweep number	Replicate	%RSD		
				$^{206}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{204}\text{Pb}$
Rhyolite	1.0	3000	2	0.82	0.67	0.90
Scoria	1.0	3000	2	0.09	0.38	0.24
Pumice	3.0	3500	2	0.40	0.29	0.07
Dacite	1.5	3000	4	0.30	0.43	0.80
Ignimbrite	2.5	3000	3	0.05	0.37	0.31
Granite	1.5	3000	5	0.43	0.32	0.33

Table 4. The accuracy of lead isotope ratios measurement compared to CRM AGV-2

Isotope ratio	Correction factor	%Recovery of AGV-2
$^{206}\text{Pb}/^{204}\text{Pb}$	1.0284	102.84
$^{207}\text{Pb}/^{204}\text{Pb}$	1.0379	103.79
$^{208}\text{Pb}/^{204}\text{Pb}$	0.9997	99.97

3.1. Acquisition Parameters at Optimum Condition

Beryllium (Be) and bismuth (Bi) solutions were introduced as internal standards to minimize signal fluctuations caused by matrix effects. This addition enhanced both the accuracy and precision of the lead isotope ratio measurements. Samples were analyzed using the collision cell device in reaction cell technology (CCT mode), which promotes ion fragmentation through collisions with a neutral gas.

The kinetic energy discrimination (KED mode) is also applied during analysis, utilizing kinetic energy differences to distinguish ions based on their atomic size. The analyte atoms differ in size from interfering species, often resulting from molecular combination reactions. The KED process selectively attenuates specific interfering ions, such as polyatomic species that compromise analytical accuracy. The integration of CCT and KED into ICP-MS marks a significant advancement in instrumentation, enhancing the precision of isotope ratio determinations compared to conventional ICP-MS systems [6, 8].

The optimal acquisition parameters varied between samples, as each matrix exhibits unique chemical characteristics and generates distinct types of interferences. Figure 1 illustrates the interrelationships between acquisition parameters during lead isotope ratio analysis using Q-ICP-MS.

Dwell time refers to the duration of the instrument when collecting a signal for a specific ion. It is depicted in Figure 1 by the time spent on the peak of the mass spectrum right before measurement. Even slight differences, measured in milliseconds, can lead to significant variations in precision because they determine the number of mass counts collected within a given time [24]. Optimal dwell time varies depending on the sample matrix, as different matrices generate distinct Pb signal intensities. In quadrupole systems, precision can be enhanced using a pseudo-simultaneous method.

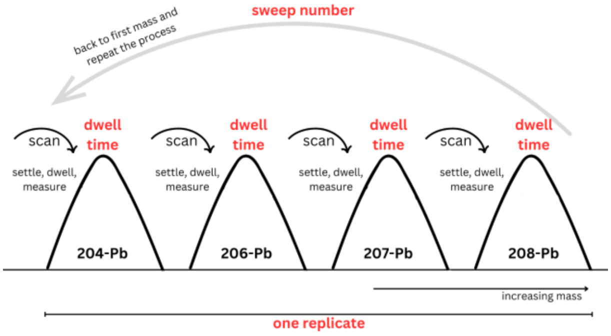

Figure 1. The connection among dwell time, sweep number, and replicate when analyzing lead isotope ratio with Q-ICP-MS (modified after Thomas [25])

Dwell times were maintained short to prevent insufficient ion counts, while keeping scanning times minimum, and allowing more sweeps during a cycle [26]. In this experiment, the required dwell times varied by rock type: rhyolite and scoria required 1 ms, dacite and granite 1.5 ms, ignimbrite 2.5 ms, and pumice 3 ms. These variations reflect the Pb concentrations in each rock; high-Pb rocks, such as rhyolite, generate an adequate signal with shorter dwell times, whereas lower-Pb rocks, such as pumice, require longer acquisition times [27].

Sweep number, defined as the total number of repeated cycles over the analyzed mass range, plays a critical role in strengthening signal intensity and improving isotopic ratio accuracy [28]. More sweep cycles enhance the stability of the final spectral peak, leading to more reliable measurements. In this study, rhyolite, scoria, dacite, ignimbrite, and granite showed optimal performance at 3000 sweeps, while pumice required 3500 sweeps to compensate for its lower Pb concentration. This highlights the need to adjust sweep numbers according to the elemental content of different rock matrices to achieve precise and accurate isotope ratio measurements [29, 30].

Replication refers to the number of times the entire sweep cycle is repeated. Increasing the number of replicates improves measurement reproducibility but also increases the consumption of reagents and sample material. Therefore, achieving an optimal balance is essential for analytical efficiency. In this study, the optimal conditions were determined as follows: two replicates for rhyolite, scoria, and pumice; three for ignimbrite; four for dacite; and five for granite.

Table 5. Lead isotope ratio concentrations of the studied samples and their reproducibility

Sample	Concentration (ppm)			Horwitz factor (PRSD$_{(R)}$)		
	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$
Rhyolite	19.37	16.56	38.31	10.18	10.43	9.19
Scoria	20.50	18.87	48.11	10.10	10.22	8.88
Pumice	21.82	19.67	50.78	10.00	10.16	8.81
Dacite	19.15	15.87	39.64	10.20	10.49	9.15
Ignimbrite	19.08	15.91	39.65	10.21	10.49	9.15
Granit	19.35	15.86	39.56	10.19	10.50	9.15

The presence of high concentrations of rare earth elements (REEs) in volcanic rock samples can significantly contribute to spectral interferences. REEs readily form polyatomic species (e.g., CeO^+, NdO^+) in the plasma, which can overlap with the mass-to-charge ratios of lead isotopes and other target analytes [31]. Samples with high REE content, such as granite and dacite, required more replicates to achieve optimal conditions. In contrast, samples with lower REE content, such as scoria and pumice, reached optimal conditions with fewer replicates [27].

3.2. Precision, Accuracy, and Reproducibility

In isotope ratio analysis using Q-ICP-MS, three analytical parameters were studied to validate the reliability of measured data. Integrating precision metrics, accuracy assessments, and Horwitz-based evaluations ensures that isotope ratio measurements are both scientifically robust and analytically defensible.

Precision refers to the degree of agreement among repeated measurements of the same sample under identical conditions and is typically expressed as the standard deviation or relative standard deviation (%RSD) [32]. In this study, precision varied across measurements, but generally, values of %RSD < 1 were achieved. As expected, lower analyte concentrations tend to increase measurement imprecision.

The highest precision was observed in the $^{206}Pb/^{204}Pb$ ratios for ignimbrite and scoria, with %RSD values of 0.05 and 0.09, respectively. The lowest precision was recorded in the $^{206}Pb/^{204}Pb$ ratios for rhyolite and dacite, with %RSD values of 0.90 and 0.80, respectively. However, these values are still considered analytically acceptable. According to AOAC International [23], the allowable %RSD is 7.3% for analyte concentrations of 10 ppm and 5.3% for 100 ppm. Since the Pb concentrations of the studied samples range from 19 to 51 ppm (Table 5), the achieved precision of 0.05–0.90% falls within acceptable limits.

Accuracy reflects how closely the measured isotope ratios align with the true or certified values, typically assessed using reference materials [33]. This assessment can be applied to individual measurements or the mean value of multiple replicates. The results of this study demonstrate acceptable accuracy and are consistent with analytical standards [34], which specifies that analytes at higher concentrations should fall within a narrower accuracy range. Given that the Pb concentrations of the studied samples range from 19 to 51 ppm (Table 4), and the measured accuracy falls between 99.97% and 103.97%, the results align well with the acceptable analytical criteria of 80–110% for 10 ppm and 90–107% for 100 ppm analyte concentrations [23].

Compared to a previous study on lead isotope ratio measurements using Q-ICP-MS [35], which reported accuracy in the range of 95–107% with an RSD below 5%, the results of this study are similarly competitive. Furthermore, the accuracy obtained here remains comparable to that achieved using sector-field ICP-MS, which typically yields 95–105% accuracy with RSD < 2%.

To benchmark the expected variability in precision across varying analyte concentrations, the Horwitz coefficient offers a widely accepted empirical guideline. It defines an acceptable level of RSD based on analyte concentration, illustrating that lower concentrations inherently tolerate higher variability. In lead isotope analysis at trace levels for geological matrices, applying the Horwitz equation helps determine whether observed precision falls within globally acceptable limits. While the consistency of replicates analyzed by the same person with the same aspects of the experiment is called repeatability, the consistency of a method used by different analysts and laboratories at other times reaches reproducibility [36].

The reproducibility value obtained from this study, 8.81–10.49, shows good compliance with the analytical criteria of Horwitz value 8 for analyte concentration of 10 ppm and 11 for 100 ppm, as guided by AOAC International [23]. A study by Ulrich *et al.* [27] on geological materials shows good lead isotope ratio results with Q-ICP-MS. The measurement of lead isotope ratios on NIST SRM 982 presented a long-term reproducibility, with the accuracy being similar to that achieved by multi-collector Q-ICP-MS, and the precision was competitive. The research concludes that determining samples with very low Pb content is permissible with Q-ICP-MS, but the lead separation must be carried out as part of the pre-treatment.

Table 6. Comparison of lead isotope ratios and %RSD of volcanic rock on different analytical techniques

Study/Source	Rock type	Location	Analytical method	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{204}\text{Pb}$	Precision (%RSD)	Note
This study	Rhyolite	Jambi, Sumatra	Optimized Q-ICP-MS	19.37	16.56	38.31	0.60-0.90	-
	Scoria			20.50	18.87	48.11	0.09-0.38	-
	Pumice			21.82	19.67	50.78	0.07-0.40	-
	Dacite			19.15	15.87	39.64	0.30-0.80	-
	Ignimbrite			19.08	15.91	39.65	0.05-0.37	-
	Granite	Bangka, Sumatra		19.35	15.86	39.56	0.32-0.43	-
Rivai *et al.* [37]	Galena	Sopokomil, Sumatra	LA-MC-ICP-MS	18.97	15.82	38.92	0.009-0.016	Ore deposit from the upper crust
Xu *et al.* [38]	Galena	Lubuk Linggau, Sumatra	LA-MC-ICP-MS	18.34-18.37	15.57-15.59	38.37-38.40	0.001-0.026	Ore from the Eocene Jangkat quartz monzonite
Li *et al.* [39]	Pyrite and galena	Cianjur, West Java	LA-MC-ICP-MS	18.55-18.65	15.55-15.68	38.52-39.01	0.002-0.118	Miocene to Pliocene volcanic rocks
Wu *et al.* [40]	Arsenopyrite, Pyrite, Galena	Ciemas, West Java	LA-MC-ICP-MS	18.79-18.89	15.70-15.77	39.18-39.42	0.002-0.11	Mineralization materials originated from the continental crust
Tessalina *et al.* [41]	Galena, cerussite, ore	Russia	MC-ICP-MS	17.43-18.11	15.48-15.63	37.20-38.02	0.12-0.22	Urals paleo-island arc zone
Wolff and Ramos [42]	Rhyolite-ignimbrite	New Mexico, USA	TIMS	17·79-17·83	15.52-15.54	37.60–37.70	~0.5-1.0	Bandelier Tuff, high-silica
Ulrich *et al.* [27]	Granitoids, amphibolites	Wyoming, USA	Q-ICP-MS	15.04-18.80	-	-	0.026-0.044	Beartooth Mountain, 2.80 Ga
	Granitoids, amphibolites	Wyoming, USA	TIMS	15.07-18.85	-	-	0.014-0.018	-
	Meteorites	-	MC-ICP-MS	10.31-18.16	-	-	0.001-0.003	-
Shafiei [43]	Eocene volcanic rocks	Iran	MC-TIMS	18.35-18.49	15.30-15.41	38.15-38.36	0.003-0.03	Kerman Cenozoic magmatic arc, fresh samples
	Ore-hosting porphyries	Iran	MC-TIMS	18.52-18.60	15.58-15.64	38.57-38.80	0.002-0.006	Kerman Cenozoic magmatic arc, hydrothermal alteration
Collerson *et al.* [44]	Hawaiian basalt	Hawaii	MC-ICP-MS	18.679	-	-	1	CRM
	Columbia River basalt	Columbia	MC-ICP-MS	18.757	-	-	1	CRM

3.3. Lead Isotope Ratios in Different Volcanic Rock Types

Lead isotope ratios ($^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, and $^{208}Pb/^{204}Pb$) are key tracers in understanding the petrogenesis and source characteristics of volcanic rocks. This study analyzed six volcanic rock types using an optimized Q-ICP-MS method. They are compared to published data for comparison, as shown in Table 6.

Table 6 presents a comparison of lead isotope ratios and the %RSD values for volcanic rock matrices analyzed in this study using Q-ICP-MS, alongside reference values obtained from other studies employing different analytical techniques. The precision observed in this study demonstrates the capability of Q-ICP-MS, under optimized conditions, to deliver reproducible lead isotope measurements with %RSD values ranging from 0.05% to 0.90%.

Laser ablation coupled with MC-ICP-MS consistently produces the highest precision, with %RSD values ranging from 0.001 to 0.009 in most studies, reflecting its superior stability and ionization efficiency. MC-ICP-MS without laser ablation gives slightly higher %RSD, which varies depending on the concentration of lead isotope ratio and the type of isotope ratio analyzed. TIMS shows even higher %RSD, even though sometimes it is coupled with MC-ICP-MS. The lead isotope ratio with Q-ICP-MS, as studied by Ulrich *et al.* [27], has better precision than this study. This is likely due to the lower Pb isotope ratio content, the limited availability of data (only showing $^{206}Pb/^{204}Pb$), and the additional pre-treatment step, in which Pb was purified using a single-stage anion exchange method eluted with HBr–HCl.

As used in this study, the implementation of collision cell technology in Q-ICP-MS significantly improves the precision, achieving %RSD values < 1.0, depending on the matrix. While LA-MC-ICP-MS remains the gold standard in isotope geochemistry, Q-ICP-MS with optimized acquisition parameters offers a cost-effective and faster alternative, suitable for high-throughput screening and regional geochemical surveys.

The variation in analytical precision among the six volcanic rock samples in this study can be attributed to differences in matrix composition, Pb concentration, and total REE content. Ignimbrite, pumice, and scoria demonstrated the highest precision, with %RSD values of 0.05-0.09 across all isotope ratios. These matrices had relatively high Pb concentrations and/or low REE contents, which are advantageous in minimizing analytical noise and spectral interferences. In contrast, granite, dacite, and rhyolite showed higher %RSD values, suggesting the presence of matrix-induced signal instability or interference.

One critical source of precision degradation in Q- ICP-MS analyses is spectral interference from polyatomic species, especially those formed by REE oxides [27]. Total REE contents in rhyolite (44.15 ppm), scoria (187.01 ppm), and pumice (80.32 ppm) were experimentally determined in this study, while literature data were used for dacite (268 ppm; [45]), ignimbrite (81-145 ppm; [46]), and granite (265 ppm; [47]). The correlation suggests that higher REE content may contribute to the formation of interfering oxide ions (e.g., NdO^+, CeO^+), which overlap with Pb mass peaks and lower the measurement precision [27]. However, rhyolite shows an anomaly. Based on theory, its precision should be higher because of the high content of Pb and the low content of REE. This discrepancy may be attributed to non-optimal sample preparation and suggests the potential need for a more intensive pre-concentration process in future analyses, particularly for rhyolite, which contains a significantly higher silica content (up to 77 wt%) than other rock types.

In addition to chemical composition, instrumental parameters and their interaction with matrix components affect reproducibility. Even with well-tuned instrument conditions, factors such as cone contamination, lens drift, and plasma instability can disproportionately influence complex matrices, especially when analyte concentrations are near detection limits. This underscores the importance of rigorous optimization, including the careful selection of dwell time, sweep number, and replicate count, all of which were empirically adjusted in this study based on sample-specific characteristics.

In conclusion, the precision of lead isotope measurements using Q-ICP-MS varies significantly across different volcanic rock types due to a combination of matrix effects, REE content, and Pb concentration. The data support the importance of tailored acquisition parameters for each rock matrix and highlight the capacity of Q-ICP-MS, when properly optimized, to yield high-quality isotopic data for geological applications.

Further optimization, such as exploring a wider range of dwell times and replicate numbers, is recommended to enhance both efficiency and precision. Reducing settling and scanning times could decrease the total integration time by 5–10 minutes, enabling more simultaneous measurements and thereby improving precision. Additional modifications may include applying a dwell time of 25 ms, increasing replicates to more than 10, and introducing oxygen or ammonia gases into the system with a flow rate of 1.0 mL/min [27, 48]. Further improvements can also be achieved through meticulous separation, enrichment, or pre-concentration of trace analytes from the bulk material using ion exchange or extraction chromatography techniques, which help to minimize isobaric interferences and matrix effects [6, 27].

3.4. Implications for Earth Science Applications

The ability to reliably measure lead isotope ratios in a wide range of volcanic rocks has broad implications in earth sciences. Accurate and precise isotope data are essential in petrogenetic studies, such as tracing magma evolution, source heterogeneity, and crustal contamination processes. Moreover, lead isotopes serve as robust tracers in environmental geochemistry, mineral exploration, and provenance studies of sediments. This information is also valuable for locating critical metals and mineral resources essential for renewable energy technology and development.

The improved precision obtained through Q-ICP-MS in this study suggests that such techniques can be applied in isotope mapping and geochronological reconstructions, especially for bulk and rapid analysis. It is also suitable for samples with moderate to high lead concentration. Furthermore, as demonstrated, careful control of acquisition parameters enhances data reliability, paving the way for broader use of isotope systems in studies related to critical metal exploration, geothermal reservoir evolution, and volcanic hazard assessment.

4. Conclusion

This study successfully optimized lead isotope ratio measurements using Q-ICP-MS for six volcanic rock matrices from Indonesia. The optimal parameters were dwell times of 1–3 ms, sweep numbers of 3000–4000, and replicates ranging from 2 to 5, depending on the rock type and Pb concentration. The method demonstrated strong analytical performance, achieving precision between 0.05% and 0.9% RSD, accuracy from 99.97% to 103.79%, and reproducibility within acceptable limits (Horwitz values of 8.8–10.5). Variations between samples were influenced by matrix composition, total rare earth element content, and SiO_2 levels, which affected signal stability and potential spectral interferences. This approach is suitable for both routine and preliminary geochemical applications.

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