

New Potential Apatite Reference Materials for Direct Sr Isotope Analysis by LA-MC-ICP-MS

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Received: February 27, 2024; Revised: April 30, 2024; Accepted: May 03, 2024; Available online: May 03, 2024.

DOI: 10.46770/AS.2024.034

ABSTRACT: High-quality Sr isotope data are critically dependent on the quality of reference materials that are used for instrumental calibration and data monitoring during LA-MC-ICP-MS analysis. Two natural apatite samples (SL-7 and SM139-1) were investigated here to test their suitability as in-situ Sr isotopic analysis reference materials. Major and trace element analyses by EPMA and LA-ICP-MS showed that apatites were all characterized by high Cl (1.80–2.46 wt%), high Sr contents (> 3752 $\mu\text{g g}^{-1}$) and extremely low Rb/Sr ratios. A total of 120 and 126 LA-MC-ICP-MS analyses for SL-7 and SM139-1 apatite showed consistent and homogeneous Sr isotopic compositions with average $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.70521 ± 0.00016 (2SD, $n = 120$) and 0.70509 ± 0.00015 (2SD, $n = 126$), respectively, which were in good agreement with solution-based data determined by TIMS or SN-MC-ICP-MS (0.705219 ± 0.000019 (2SD, $n = 13$) and 0.705114 ± 0.000041 (2SD, $n = 13$), respectively), suggesting that SL-7 and SM139-1 apatites can be used as potential reference materials for microbeam Sr isotopic analysis.

INTRODUCTION

Apatite ($\text{Ca}_5\text{PO}_4\text{F}$), a common accessory mineral occurring in magmatic rocks and sediments, has received increasing interest over the last two decades. It can be dated with the U–Th–Pb method, and the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio remains unchanged since its crystallization due to the negligible ingrowth of ^{87}Sr from the radiogenic decay of ^{87}Rb .^{1,2} Therefore, apatite has become a mineral of choice besides zircon in crustal evolution studies. Additionally, the mobility of Sr with fluids can be used to investigate fluid dynamics in magmatic-hydrothermal systems, such as the fluid-rock interactions in V-Ti-Fe oxide-apatite deposits.³

A state-of-the-art analytical technique is a prerequisite for the aforementioned geological applications. For Sr isotope analysis, bulk methods, such as thermal ionization mass spectrometry (TIMS) and solution nebulizer multiple collector-inductively coupled plasma mass spectrometry (SN-MC-ICP-MS), providing highly precise and accurate analysis, but consume more sample with rigorous and time-consuming sample preparation, as well as a limited spatial resolution. In-situ techniques have been developed rapidly in the past decades and has a high spatial resolution, high efficiency, and less time-consuming sample preparation. However, its accuracy largely relies on the quality and availability of well-characterized reference materials (RMs). The reported apatite reference materials for Sr isotope analysis show either low REE (Slyudyanka apatite, < 500 $\mu\text{g g}^{-1}$) or high REE

contents (MAD, > 7000 $\mu\text{g g}^{-1}$) (Table S1). A similar matrix composition and mass fraction of the element of interest of the RM and the unknown sample are preferable, which can be called matrix matched.⁴

In this study, two apatite samples (REE, $\sim 3000 \mu\text{g g}^{-1}$) were developed and the major and trace element compositions were examined using electron probe microanalyzer (EPMA) and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). The following Sr isotopic characteristics of the homogeneity test on the micrometer scale using LA-MC-ICP-MS and intergranular scale using TIMS or SN-MC-ICP-MS were compared and evaluated for their potential as reference materials for direct Sr isotopic analysis.

EXPERIMENTAL

Sample description and preparation. The apatite samples were collected from Eppawala in north-central Sri Lanka, where developed a number of economically important phosphate deposits.⁵ These phosphate deposits formed as residual products of tropical weathering of an apatite-bearing carbonate unit within the local basement complex which consists mainly of high-grade metamorphic rocks. The majority of apatite crystals from carbonate rocks at Eppawala are fresh and unfractured. Commonly, they have sharp contacts with the surrounding carbonate matrix, but sometimes they appear to be replaced by carbonates along their margins.^{6,7} The Eppawala apatite crystals show as primary greenish chlor-fluor-hydroxyl of maximum diameter varying from a few mm and sometimes exceeding 1 m (Fig. 1). According to SEM analysis, these apatites were pure and appeared to be free of zonation and inclusions, and then were tested for homogeneity of major elements by EPMA and trace elements followed by LA-ICP-MS analysis. After that, two apatite samples were selected and crushed to around 3 kg of clean apatite fragments. More than 20 apatite fragments were mounted in epoxy and polished for direct microanalysis. Two grams of apatite separate from each sample were grounded to 200 mesh and distributed to three laboratories for bulk Sr isotopic analysis.

Major element analysis by EPMA. Major elements in apatite were determined using a JEOL-JAX8100 EPMA instrument equipped with a tungsten filament at EPMA and SEM laboratory, Institute of Geology and Geophysics, Chinese Academy of Sciences (IGGCAS). The accelerating voltage was set to 15 kV and the beam current were 20 nA, with a beam diameter of 5 μm . The following spectral lines were monitored: Na $K\alpha$, Mg $K\alpha$, Al $K\alpha$, and Sr $K\alpha$ with the TAP diffracting crystal, Cr $K\alpha$, Mn $K\alpha$, Fe $K\alpha$, Co $K\alpha$, and Ni $K\alpha$ with the LIFH diffracting crystal, K $K\alpha$, Ca $K\alpha$, and Ti $K\alpha$ with the PETJ diffracting crystal. Natural minerals and synthetic oxides were used for calibration as

Fig. 1 Outcrop photographs of the apatite in Eppawala carbonatites and the hand specimen.

followers: albite (Na and Al), diopside (Ca, Si and Mg), K-feldspar (K), celestine (Sr), rutile (Ti), Fe_2O_3 (Fe), and apatite (Ca, P, F, and Cl). The counting time was 10-20 s for major and trace elements.⁸ The background count time for each element was set to half the peak count time. Detection limits were (3s) 0.03% m/m for K, Mg, Ca, and Al, 0.06% m/m for Na, Cr, Si, Mn, Fe, Co, and Ti, and 0.08% m/m for Sr, Ba and Ni, respectively. To minimize possible losses of alkali metals (especially Na) during measurement, these elements were first to be determined. The overall analytical bias was typically < 2% for elements at mass fraction level of 2% m/m oxide (Table S2). A program based on ZAF procedure was applied for data corrections.⁹

Trace element analysis by LA-ICP-MS. The trace elements of apatite were determined by a 193 nm ArF Excimer laser (GeoLas Pro, Coherent) coupled with an Element XR SF-ICP-MS instrument (Thermo Fisher, USA) at the Metallogenic Elements and Isotopes Laboratory, IGGCAS. Ablation was performed in a He-Ar mixture. The analyses were conducted using a 44- μm spot diameter, 5 Hz frequency and 5 J cm^{-2} energy density during a 90-s analysis (20 s for the gas blank, 40 s on the chromite and 30 s washout). NIST SRM 610 was used for external calibration, and BCR-2G and BIR-1G standards were analyzed as unknowns during each analytical run to check the accuracy and precision of the analyses. Off-line data processing was performed with the GLITTER program using Ca as an internal standard.¹⁰ For most trace elements (> 0.10 $\mu\text{g g}^{-1}$), the systematic bias was better than $\pm 10\%$ with the relative standard deviation of $\pm 10\%$ (Table S3).

Sr isotopic analysis by LA-MC-ICP-MS. Direct Sr isotope measurements were performed using Neptune Plus MC-ICP-MS (Thermo Scientific, USA), coupled with a 193 nm ArF excimer laser ablation system (Analyte G2, Teledyne CETAC, Technologies, USA) at the State Key Laboratory of Lithospheric Evolution, IGGCAS, following the method of Yang *et al.*¹¹ A spot diameter of 44 μm with a repetition rate of 8 Hz and an energy

Table 1. Operating parameters for Sr isotopic measurements by LA-MC-ICP-MS

MC-ICP-MS (Neptune Plus)	
RF power	1300 W
Cooling gas flow rate	18.0 L min ⁻¹
Auxiliary gas flow rate	0.8 L min ⁻¹
Argon make-up gas flow rate	0.9 L min ⁻¹
Nitrogen gas flow rate	4 mL min ⁻¹
Interface cones	Standard sample cone + X skimmer cone
Instrument resolution	Low resolution
Analysis mode	Static
Detection system	Nine Faraday collectors
Collector configuration	L4 (⁸³ Kr), L3 (¹⁶⁷ Er ²⁺), L2 (⁸⁴ Sr), L1 (⁸⁵ Rb), C (⁸⁶ Sr), H1 (¹⁷³ Yb ²⁺), H2 (⁸⁷ Rb + ⁸⁷ Sr), H3 (⁸⁸ Sr)
Integration time	0.262 s, one block of 200 cycles
Laser ablation system (Analyte G2)	
Laser type	ArF excimer laser
Wavelength	193 nm
Pulse length	4 ns
Energy density	5 J cm ⁻²
Ablation mode	Single spot
Spot diameter	44 μm
Repetition rate	8 Hz
Helium carrier gas flow rate	0.8 L min ⁻¹

density of 5 J cm⁻² was applied for apatite samples. All analyses were performed in static mode with low mass resolution using Faraday cups equipped with 10¹¹ Ω resistors. Gain calibration was performed daily. Instrument parameters were optimized carefully using an NBS 987 standard solution to obtain the best peak shape and maximum sensitivity. An X skimmer cone was used to improve signal intensity.¹² A small amount of N₂ (4 mL min⁻¹) was added to the helium carrier gas (~0.8 L min⁻¹) and mixed with the argon make-up gas (~0.9 L min⁻¹) before it entered the ICP-MS to improve sensitivity and suppress isobaric interference.¹³ An individual data acquisition consisted of one block of 200 cycles with an integration time of 0.262 s per cycle. Each spot analysis started with a 13 s Kr gas blank correction, followed by 40 s ablation for signal acquisition and another 30 s for signal wash out (Table 1).

The interference of ⁸⁴Kr and ⁸⁶Kr on ⁸⁴Sr and ⁸⁶Sr, respectively, was reduced by the ~13 s Kr gas blank measurement using the natural Kr isotopic ratios (⁸³Kr/⁸⁴Kr = 0.20175, ⁸³Kr/⁸⁶Kr = 0.66474).^{14, 15} The potential ion isobaric interference of doubly charged Er²⁺ and Yb²⁺ was evaluated and corrected by monitoring the intensities of interference-free ¹⁶⁷Er²⁺ (m/z = 83.5) and ¹⁷³Yb²⁺ (m/z = 86.5).¹⁶ The natural ratio of ⁸⁵Rb/⁸⁷Rb = 2.5926 was employed to correct for isobaric interference of ⁸⁷Rb on ⁸⁷Sr using the exponential law, assuming that Rb has the same mass discrimination behavior as Sr.¹⁷ Finally, the ⁸⁷Sr/⁸⁶Sr ratios were calculated and normalized from the interference-corrected ⁸⁶Sr/⁸⁸Sr ratio (⁸⁶Sr/⁸⁸Sr = 0.1194) using the exponential law. The whole data reduction procedure was performed offline using an in-house Excel macro program following the procedure reported by Yang *et al.*¹⁸ The well-characterized Slyudyanka apatite reference material was used for data quality control during direct Sr isotope analysis, yielding mean ⁸⁷Sr/⁸⁶Sr ratios of 0.70778 ± 0.00027 (2SD,

n = 18), which is consistent with recommended values of 0.70769 ± 0.00015.¹¹

Solution Sr isotopic analysis by TIMS and SN-MC-ICP-MS.

The bulk Sr isotopic ratios of apatite were obtained using standard digestion and chemical purification with TIMS at IGGCAS, the Institute of Geology of the Chinese Academy of Geological Sciences, Beijing (IGCAGS) and the Key Laboratory of Uranium Geology, China Geological Survey, Tianjin (CGST), respectively, and SN-MC-ICP-MS technique at IGCAGS. All the ⁸⁷Sr/⁸⁶Sr ratios were normalized to ⁸⁸Sr/⁸⁶Sr = 8.375209 using the exponential law for mass fractionation correction. A brief description of the analytical procedure is given below.

TIMS (IGGCAS). The Sr isotopic analysis followed procedures similar to those described by Li *et al.*¹⁹ Whole rock powders for Sr isotopic analysis were dissolved in Savillex Teflon screw-top capsule prior to HF + HNO₃ + HClO₄ dissolution. Sr was separated using the classical two-step ion exchange chromatographic (AG50W-X12) method and measured using a Thermo Fisher Scientific Triton Plus multi-collector thermal ionization mass spectrometer at IGGCAS. The whole procedure blank was lower than 240 pg for Sr. The international standard sample NBS-987 was employed to evaluate instrument stability during the period of data collection. The measured value for the NBS-987 Sr standard were ⁸⁷Sr/⁸⁶Sr = 0.710260 ± 0.000012 (2 times standard error (2SE)). USGS reference material BCR-2 was measured to monitor the accuracy of the analytical procedures, with the following result: ⁸⁷Sr/⁸⁶Sr = 0.705018 ± 0.000012 (2SE). The ⁸⁷Sr/⁸⁶Sr data of BCR-2 show good agreement with previously published data by TIMS technique.¹⁹

TIMS (CGST). For each sample, four aliquots were dissolved in

a 7 mL Savillex PFA vials with a mixed acid of 2.5 mL HF + 0.5 mL HNO₃ + 0.15 mL HClO₄ at 150 °C on a hot plate for 7 days and then dried down. After re-dissolved with 2 mL HCl and dried down, 2 mL HF acid was added to the vial to form a fluoride precipitate containing Sr and kept at 100°C for 2 h. The fluoride precipitate was transferred into a 7 mL Savillex Teflon PFA vial and dissolved with 2 mL HCl and 1 mL 3% H₃BO₃ solution, which was then evaporated to dryness. Finally, the precipitate was dissolved with 1 mL 2.5 M HCl and loaded onto the preconditioned cation exchange column (AG50W-X12) for Sr separation.²⁰ ⁸⁷Sr/⁸⁶Sr ratios were measured by a Thermo Fisher Scientific Triton TIMS instrument. The Sr isotope ratios were determined using a double Re filament geometry. During Sr isotope analysis, 1 µL of 0.15 M H₃PO₄ was loaded onto a Re filament and dried slowly at 0.8 A as an ionization activator. The measurement data consisted of 15 blocks, each of which contained 10 cycles of a 4 s integration (Table S4). The NIST SRM 987 standard and BCR-2 were used to monitor the status of TIMS and the values of ⁸⁷Sr/⁸⁶Sr were 0.710263 ± 0.000003 (2SE) and 0.705012 ± 0.000007 (2SE), which were in good agreement with previously reported values.^{21,22}

TIMS (IGCAGS). For each sample, three aliquots were dissolved in Savillex beakers with a mixed acid of HNO₃ + HF, and then transferred into HNO₃ and HCl solution in turn. The Sr chemical separation followed standard ion exchange procedures, employing AG50W-X12 (200-400 mesh) cation exchange resin. ⁸⁷Sr/⁸⁶Sr ratios were measured by a Finnigan MAT262 TIMS instrument equipped with a multi-collector consisting of six separate cups. The NIST SRM 987 standard and BCR-2 were used to monitor the status of TIMS and the values of ⁸⁷Sr/⁸⁶Sr were 0.710256 ± 0.000014 (2SE) and 0.705011 ± 0.000012 (2SE), which were in good agreement with previously reported values.^{21,22}

SN-MC-ICP-MS (IGCAGS). The sample dissolution and chemical separation followed the descriptions aforementioned in TIMS, IGCAGS. ⁸⁷Sr/⁸⁶Sr ratios were measured by a Nu Plasma HR MC-ICP-MS equipped with twelve Faraday cups. The NIST SRM 987 standard and BCR-2 were used to monitor the status of TIMS and the values of ⁸⁷Sr/⁸⁶Sr were 0.710244 ± 0.000012 (2SE) and 0.704993 ± 0.000014 (2SE), which were in good agreement with previously reported values.^{21,22}

RESULTS AND DISCUSSION

Major and trace element compositions of apatite

SL-7 apatite. Fifty-nine EPMA and one hundred and fifty-six LA-ICP-MS spot analyses were performed on randomly selected grains to determine the chemical compositions. The individual analytical results are listed in Tables S2 and S3. The average major and trace element compositions are listed in Table 2. EPMA results

Table 2. Summary of major (wt%) and trace (ppm) element compositions of apatite analyzed by EPMA and LA-ICP-MS

Element	SL-7 Apatite				SMI39-1 Apatite			
	Value	SD	Min	Max	Value	SD	Min	Max
FeO	0.13	0.03	0.07	0.18	0.07	0.03	0.00	0.16
MnO	0.03	0.02	0.00	0.08	0.02	0.02	0.00	0.07
MgO	0.34	0.07	0.16	0.60	0.16	0.07	0.00	0.32
CaO	55.1	0.6	52.8	55.8	55.9	0.3	55.0	56.7
SrO	0.20	0.03	0.14	0.31	0.21	0.04	0.13	0.34
Na ₂ O	0.18	0.04	0.10	0.26	0.17	0.05	0.00	0.33
P ₂ O ₅	40.8	0.6	39.0	42.0	40.5	0.5	39.6	41.6
Cl	2.14	0.12	1.88	2.46	2.07	0.12	1.80	2.45
F	2.18	0.15	1.92	2.62	2.06	0.11	1.66	2.55
Na	1190	67	1001	1319	1175	44	1049	1279
Mg	1640	288	1057	2365	989	290	458	1660
Si	962	94	750	1282	1003	57	773	1189
Mn	204	12	156	225	155	17	120	193
Fe	801	127	472	1001	448	62.1	336	619
Rb	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
Sr	4175	92	3844	4343	4047	76	3752	4234
Y	71.1	2.3	66.6	83.7	65.4	3.8	51.1	73.4
Zr	3.14	0.27	2.41	3.78	2.17	0.32	1.19	2.80
Nb	0.05	0.01	0.03	0.08	0.04	0.01	0.02	0.07
Ba	35.5	6.8	13.0	52.0	29.2	4.3	14.8	45.6
La	564	21	514	638	558	32	488	738
Ce	1305	45	1204	1491	1302	55	1189	1603
Pr	167	6	154	193	163	6	152	197
Nd	695	25	647	813	658	33	559	793
Sm	100	4	92.6	118	94.4	5	79.4	111
Eu	17.8	0.7	16.4	21.1	17.1	1.1	15.0	23.8
Gd	50.2	1.8	46.9	58.3	46.9	2.4	38.7	52.8
Tb	4.46	0.17	4.10	5.32	4.30	0.23	3.55	4.80
Dy	18.6	0.7	17.2	21.9	17.7	1.0	14.1	20.0
Ho	2.67	0.10	2.46	3.10	2.53	0.14	2.01	2.80
Er	5.72	0.23	5.31	6.87	5.55	0.32	4.38	6.21
Tm	0.61	0.03	0.56	0.72	0.59	0.04	0.47	0.68
Yb	3.21	0.18	2.84	3.99	3.05	0.19	2.45	3.45
Lu	0.40	0.02	0.35	0.46	0.37	0.03	0.29	0.44
Pb	7.12	1.20	5.64	16.9	7.77	0.46	6.88	8.95
Th	72.3	3.7	63.9	88.4	90.8	6.5	71.7	103
U	4.82	0.27	4.18	5.77	5.50	0.26	4.62	6.28

bdl represents below detection limit.

show that these apatites have similar and homogeneous major element compositions with limited ranges of 52.8-55.8 wt% CaO and 39.0-42.0 wt% P₂O₅, with an average value of 55.1 ± 0.6 wt% and 40.8 ± 0.6 wt% (standard deviation (SD), n = 59), respectively. The mean value of F and Cl is 2.14 ± 0.12 wt% and 2.18 ± 0.15 wt% (SD, n = 59), respectively. The accuracy of most trace elements was better than 10% with an analytical precision of 10% (1 relative standard deviation). The average content of Sr is 4175 ± 92 µg g⁻¹ (SD, n = 156), whereas Rb is below the detection limit (< 0.06 µg g⁻¹).

SMI39-1 apatite. One hundred and eighteen EPMA and two hundred and fourteen LA-ICP-MS spot analyses were performed to determine the chemical compositions. EPMA results show the SMI39-1 apatite span a range from 55.0 to 56.7 wt% for CaO and 39.6 to 41.6 wt% for P₂O₅, with an average value of 55.9 ± 0.3 wt% and 40.5 ± 0.5 wt% (SD, n = 118), respectively. The mean value

Fig. 2 LA-MC-ICP-MS $^{87}\text{Sr}/^{86}\text{Sr}$ measurements of SL-7 (a and b) and SM139-1 (c and d). The error bars are 2SE for individual analysis. Red dashed lines are the mean values, and grey shaded regions represent 2SD of the mean values.

Fig. 3 TIMS and SN-MC-ICP-MS Sr isotopic measurements of SL-7 and SM139-1. Blue, green and purple circles represent data obtained using TIMS at IGGCAS, CGST and IGCAGS, respectively. Diamonds represent data obtained using SN-MC-ICP-MS at IGCAGS. The red dashed lines represent the mean values and the grey shades represent 2SD around the mean values. Red circles represent the combined mean values of MC-ICP-MS and TIMS. The error bars are 2SE for individual values.

of F and Cl is 2.07 ± 0.13 wt% and 2.06 ± 0.11 wt% (SD, $n = 118$), respectively. The average content of Sr is 4047 ± 76 $\mu\text{g g}^{-1}$ (SD, $n = 214$), whereas Rb is below the detection limit (< 0.06 $\mu\text{g g}^{-1}$). In general, the two apatite samples are characterized by extremely low contents of Rb (very low Rb/Sr ratios). Hence, isobaric interference of ^{87}Rb on ^{87}Sr is usually insignificant and can be negligible for direct Sr isotopic analysis of the SL-7 and SM139-1 apatite samples.

Sr isotopic compositions of apatite by LA-MC-ICP-MS. In situ Sr isotopic data of apatite SL-7 and SM139-1 were obtained under optimized instrumental conditions by LA-MC-ICP-MS. The individual analytical results are listed in Table S5. 120 analyses of randomly selected SL-7 apatite fragments and 126 analyses of SM139-1 fragments were performed to investigate the homogeneity of Sr isotopes and yielded mean $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.70521 ± 0.00016 (2SD, $n = 120$) and 0.70509 ± 0.00015 (2SD, $n = 126$) (Fig. 2 and Table S5), respectively. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the two apatites range from 0.70501 to 0.70545 and 0.70492 to 0.70530, both following the Gaussian distribution and the twice

Table 3. Summary of Sr isotope ratios for geological reference materials (RMs) and apatite by TIMS, SN-MC-ICP-MS or LA-MC-ICP-MS

Sample	$^{87}\text{Sr}/^{86}\text{Sr}$	Uncertainty	Number	Methods	Instrument	Lab	<i>p</i>
RMs measured by solution-based methods							
SRM 987	0.710260	0.000012 (2SE)	1	TIMS	Triton Plus	IGGCAS	
	0.710263	0.000003 (2SE)	1	TIMS	Triton	CGST	
	0.710256	0.000014 (2SE)	1	TIMS	MAT 262	IGCAGS	
	0.710244	0.000012 (2SE)	1	SN-MC-ICP-MS	Nu Plasma	IGCAGS	
	0.705018	0.000012 (2SE)	1	TIMS	Triton Plus	IGGCAS	
BCR-2	0.705012	0.000007 (2SE)	1	TIMS	Triton	CGST	
	0.705011	0.000012 (2SE)	1	TIMS	MAT 262	IGCAGS	
	0.704993	0.000014 (2SE)	1	SN-MC-ICP-MS	Nu Plasma	IGCAGS	
Apatite measured by solution-based methods							
SL-7	0.705217	0.000016 (2SD)	3	TIMS	Triton Plus	IGGCAS	
	0.705220	0.000017 (2SD)	4	TIMS	Triton	CGST	
	0.705231	0.000008 (2SD)	3	TIMS	MAT 262	IGCAGS	
	0.705209	0.000004 (2SD)	3	SN-MC-ICP-MS	Nu Plasma	IGCAGS	
Average	0.705219	0.000019 (2SD)	13				4
SM139-1	0.705124	0.000015 (2SD)	3	TIMS	Triton Plus	IGGCAS	
	0.705093	0.000041 (2SD)	4	TIMS	Triton	CGST	
	0.705134	0.000015 (2SD)	3	TIMS	MAT 262	IGCAGS	
	0.705112	0.000023 (2SD)	3	SN-MC-ICP-MS	Nu Plasma	IGCAGS	
Average	0.705114	0.000041 (2SD)	13				4
Apatite measured by LA-MC-ICP-MS							
SL-7	0.70521	0.00016 (2SD)	120	LA-MC-ICP-MS	G2 + Neptune Plus	IGGCAS	
SM139-1	0.70509	0.00015 (2SD)	126	LA-MC-ICP-MS	G2 + Neptune Plus	IGGCAS	

standard deviation is comparable to the mean value of internal precision (0.00010), indicating good Sr isotopic homogeneity of the SL-7 and SM139-1 apatites at 44 μm sampling scale and appear to lack significant inter-grain variations.

Sr isotopic compositions of apatite by TIMS or SN-MC-ICP-MS. For comparison, solution Sr isotopic compositions of apatite SL-7 and SM139-1 were determined by different laboratories using TIMS or SN-MC-ICP-MS techniques. Results of four laboratories are given in Table 3, Table S6 and Fig. 3.

SL-7 apatite. Three analyses yielded an average $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.705217 ± 0.000016 (2SD, $n = 3$) using TIMS at IGGCAS and four analyses yielded an average $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.705220 ± 0.000017 (2SD, $n = 4$) using TIMS at CGST. Three analyses yielded an average $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.705231 ± 0.000008 (2SD, $n = 3$) using TIMS and 0.705209 ± 0.000004 (2SD, $n = 3$) using SN-MC-ICP-MS at IGCAGS (Table 3 and Fig. 3).

SM139-1 apatite. Analyses yielded an average $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.705124 ± 0.000014 (2SD, $n = 3$), 0.705093 ± 0.000041 (2SD, $n = 4$) and 0.705134 ± 0.000015 (2SD, $n = 3$) using TIMS at IGGCAS, CGST and IGCAGS, respectively (Table 3). Three analyses yielded an average $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.705112 ± 0.000023 (2SD, $n = 3$) using SN-MC-ICP-MS at IGCAGS (Fig. 3).

The recommended values for potential apatite reference materials. Data quality was checked by careful evaluation and verification of the calibration procedures and analytical techniques, such as the calibration procedure and the verification of analytical

techniques by measurements of quality control materials (Table 3). Results obtained by different instrument (TIMS and MC-ICP-MS) or from different laboratories are generally in good agreement, and therefore no data were identified as outliers. T-test with dissimilar variances were employed to compare the LA-MC-ICP-MS and solution-based TIMS and MC-ICP-MS values. The results (SL-7, $P_{\text{two-tail}} = 0.34 > 0.05$; SM139-1, $P_{\text{two-tail}} = 0.014 < 0.05$) show that LA-MC-ICP-MS commonly suffers from matrix effects, which data quality are related to the reference material used for calibration, and thus was excluded from the calculation of recommended value. As the small number of laboratories ($p = 4$, p denotes the number of laboratories), we report the mean values of data as preliminary reference values. Thirteen aliquots of apatite solutions determined by TIMS or SN-MC-ICP-MS at four labs gave consistent results with an unweighted mean of $^{87}\text{Sr}/^{86}\text{Sr} = 0.705219 \pm 0.000019$ (2SD, $n = 13$) and 0.705114 ± 0.000041 (2SD, $n = 13$), respectively (Table 3 and Fig. 3).

CONCLUSION

In this study, the homogeneity of two natural high Cl apatite RMs for in-situ Sr isotopic analysis by LA-MC-ICP-MS were characterized and the recommended isotopic compositions were determined using TIMS or SN-MC-ICP-MS. The results indicated that the SL-7 and SM139-1 apatite can be used as reference materials for in-situ Sr isotopic analysis with $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of 0.70521 ± 0.00016 (2SD, $n = 120$, LA-MC-ICP-MS) and 0.70509 ± 0.00015 (2SD, $n = 126$, LA-MC-ICP-MS), respectively.

These apatite fragments are available upon request (wangjing@mail.iggcas.ac.cn) as set of 3-5 apatite fragments (fraction 0.5-1 mm).

ASSOCIATED CONTENT

Supporting information (Tables S1–S6) is available at www.at-spectrosc.com/as/home.

AUTHOR INFORMATION



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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This study was financially supported by the National Natural Science Foundation of China (42303047) and the Instrument Function Development Technology Innovation Project of Chinese Academy of Sciences.

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