In situ Rb-Sr Dating of Lunar Meteorites Using Laser Ablation MC-ICP-MS

Wen Zhang,^{a,*} Zaicong Wang,^a Zhaochu Hu,^a Qi He,^a Yiheng Li,^a Yangtong Feng,^a
Hong Liu,^a and Xiaojing Zhang^b

^a State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences, Wuhan 430074, P.R. China

^b Qianxuesen Laboratory of Space Technology, China Academy of Space Technology, Beijing 100029, P.R. China

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ABSTRACT: Plagioclase, pyroxene and glass are the main component phases of different planetary materials. *In situ* Rb-Sr dating of these common phases thus would represent the timing of magmatic differentiation, effectively complementary to the rare, tiny U-Pb bearing phases that only form at a late stage. In this study, we selected lunar meteorites as examples to establish an *in situ* Rb-Sr dating method where plagioclase, pyroxene, ilmenite, and glasses were the laser-ablation (LA) targets. The accuracy of $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{87}\text{Rb}/^{86}\text{Sr}$ measured by LA-MC-ICP-MS was better than 0.2 ‰ and 3 ‰, respectively, for samples with an $^{87}\text{Rb}/^{86}\text{Sr}$ ratio lower than 1. However, we found that the distributions of Rb and Sr in the natural materials were heterogeneous at the micrometer scale, leading to inaccurate $^{87}\text{Rb}/^{86}\text{Sr}$ ratio correction when calculated by normal data reduction methods. A new data reduction strategy of the smallest unit of isochron age (SUIA) was developed. Using the SUIA, the Rb-Sr isochron age of 2984 ± 43 Ma and 3149 ± 20 Ma was obtained for two lunar meteorites (NWA 10597 and NWA 6950, respectively). These results are identical within 1-2% deviation relative to the U-Pb dating ages for baddeleyite and apatite using SIMS. The present method may have broad applicability for determining the Rb-Sr isochron ages of other planetary samples.

In situ Rb-Sr dating by LA-MC-ICP-MS for Lunar meteorites

INTRODUCTION

The Rb-Sr decay system was one of the first and extensively used methods for geochronology studies.^{1, 2} ^{87}Rb decays to ^{87}Sr by β decay with a decay constant of $1.393 \pm 0.004 \times 10^{-11}$ per year.³ An advantage of the Rb-Sr system is the relatively large variation of the Rb/Sr ratio in rocks, largely due to the difference in the geochemical properties between Rb and Sr. The system has been successfully applied to igneous rocks, metamorphic rocks, and sulfide minerals in ore deposits.⁴⁻⁶

The accurate determination of $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{87}\text{Rb}/^{86}\text{Sr}$ for Rb-Sr dating is generally conducted by thermal ionization mass spectrometry (TIMS) or multicollector inductively coupled plasma mass spectrometry (MC-ICP-MS) in combination with a complex chemical purification process and isotopic spiking. In

recent years, an *in situ* Rb-Sr dating method was developed based on laser ablation inductively coupled plasma mass spectrometry/mass spectrometry (LA-ICP-MS/MS).⁷⁻¹⁰ ICP-MS/MS can effectively resolve the isobaric interference of ^{87}Rb on ^{87}Sr by using a reaction/collision cell to separate Rb and Sr.¹¹ Hence, LA-ICP-MS/MS allows for targeted analysis at the micrometer scale, making *in situ* Rb-Sr dating of minerals possible. The most popular ICP-MS/MS instrument currently in use is the Agilent 8800, which is a quadrupole ICP-MS/MS. However, recently, the Vienna MC-ICP-MS/MS was introduced (manufactured by Thermo Scientific) and used by Craig *et al.*¹² for *in situ* Rb-Sr dating, combined with a laser ablation system. During the measurements by traditional (MC-)ICP-MS without the reaction/collision cell, the ^{87}Rb interference is corrected by monitoring ^{85}Rb and using the natural $^{87}\text{Rb}/^{85}\text{Rb}$ ratio of 0.38571.

Fig. 1 The modelled effects of variable $^{87}\text{Rb}/^{86}\text{Sr}$ ratios on radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ at different crystallization ages (1000 Ma, 2000 Ma, 3000 Ma, 4000 Ma). The black line represents an accumulated value of 0.001 for $^{87}\text{Sr}/^{86}\text{Sr}$, which can be resolved using the latest developed LA-MC-ICP-MS instrument, but is difficult to resolve with the quadrupole ICP-MS/MS.

This correction approach, however, may lead to inaccurate results when the concentration of the interfering element (in this case, Rb) is too high.¹³

The formation ages of lunar materials, including lunar meteorites and lunar samples collected during space missions, are critical for establishing the evolution history of the Earth-Moon system.^{14, 15} Whole rock / mineral solution Rb-Sr isotope data have been obtained to determine the age of lunar meteorites,^{16, 17} but these rarely involved the micro-analysis method. The micro-analysis technique requires only a tiny amount of sample and, more importantly, can achieve high-spatial resolution. *In situ* U-Pb dating has been widely used for such purposes, but this method targets U-Pb rich phases, such as baddeleyite and apatite, which mainly form at the late stage of magmatic differentiation.^{18, 19} However, most meteorites are ultramafic or mafic in composition and U-Pb rich phases therein are rare or, if any, are tiny.

Instead, plagioclase, pyroxene and glass are the main constituent phases of different planetary samples. *In situ* dating of these widely present phases is significant for planetary magmatism, and the Rb-Sr system would be ideal and represent the timing of magma differentiation. More importantly, these minerals in meteorites generally display low but highly variable Rb/Sr ratios. The variable Rb/Sr ratios in plagioclase, pyroxene and glasses could be suitable for isochron. However, the low Rb/Sr minerals do not accumulate significant radiogenic ^{87}Sr , even in old meteorites. Fig. 1 shows the radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ ratios from different $^{87}\text{Rb}/^{86}\text{Sr}$ ratios. The 0.001 change of $^{87}\text{Sr}/^{86}\text{Sr}$ caused by ^{87}Rb decay can be identified by using the modern LA-MC-ICP-MS method, but it is difficult with quadrupole ICP-MS/MS.

In this study, we investigate the potential of *in situ* Rb-Sr dating by LA-MC-ICP-MS of lunar meteorites. The accuracy and precision of $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{87}\text{Rb}/^{86}\text{Sr}$ are assessed in detail through repeated analysis of 14 reference materials. Plagioclases, pyroxenes, ilmenites, and glasses in two lunar meteorites (NWA 10597 and NWA 6950) were measured by LA-MC-ICP-MS. We developed a new data reduction method to resolve the heterogeneous distribution of Rb and Sr in natural minerals. The final Rb-Sr isochron age of the two meteorites was found to be consistent with the results obtained using other radiogenic dating systems.

EXPERIMENTAL

Instrumentation. *In situ* Sr isotope analyses were performed with the NEPTUNE Plus MC-ICP-MS instrument (Thermo Fisher Scientific, Bremen, Germany), which was connected to a femtosecond laser ablation system located at the State Key Laboratory of Geological Processes and Mineral Resources (GPMR), China University of Geosciences, Wuhan. The NEPTUNE Plus, which is a double focusing MC-ICP-MS, was equipped with seven fixed electron multiplier ICs and nine Faraday cups fitted with $10^{11} \Omega$ resistors. The Faraday collector configuration of the mass system was composed of an array from L4 to H3 to monitor Kr, Rb, Er, Yb, and Sr (Table 1). The femtosecond laser ablation system is a NWR Femto^{UC} femtosecond system (New Wave Research, Fremont, CA, USA), which consisted of a 300 fs Yb: KGW femtosecond laser amplifier (PHAROS, Light Conversion Ltd., Vilnius, Lithuania) with a wavelength of 257 nm. The laser ablation was equipped with a two-volume cell, which has the constant distance between the laser

Table 1 Summary of the operating parameters for LA-MC-ICP-MS

MC-ICP-MS (Neptune Plus)	Parameters
RF power	1250 W
Cool gas flow	16.0 L min ⁻¹
Auxiliary gas flow	0.80 L min ⁻¹
Helium carrier gas flow	0.90 L min ⁻¹
Nitrogen gas flow	12 ml min ⁻¹
Interface cones	X skimmer cone + Jet sample cone
Instrument resolution	~ 400 (low mode)
Block number	1
Cycles of each block	120
Integration Time (s)	0.524 s
Cup-configuration	L4 (^{83}Kr), L3 ($^{167}\text{Er}^{++}$), L2 (^{84}Sr), L1 (^{85}Rb), C (^{86}Sr), H1 ($^{173}\text{Yb}^{++}$), H2 (^{87}Sr), and H3 (^{88}Sr).
Laser ablation system	Parameters
Laser type	Yb: YAG femtosecond laser
Wavelength	257 nm
Pulse length	300 fs
Energy density	60%
Spot size	50-60 μm
Laser frequency	10-30 Hz
Scan speed	2-6 $\mu\text{m s}^{-1}$

Table 2 The measurement results of $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{87}\text{Rb}/^{86}\text{Sr}$ by LA-MC-ICP-MS for 14 reference materials

Reference materials	Recommended values					Measured values by LA-MC-ICP-MS						
	Rb ($\mu\text{g g}^{-1}$)	Sr ($\mu\text{g g}^{-1}$)	$^{87}\text{Rb}/^{86}\text{Sr}$	$^{87}\text{Sr}/^{86}\text{Sr}$	uncertainty	$^{87}\text{Rb}/^{86}\text{Sr}$	2SD	Rel. error (%) *	$^{87}\text{Sr}/^{86}\text{Sr}$	2SD	Rel. error (%) #	N
NIST610	415	521	2.320	0.70970	0.00002	2.251	0.015	-2.97	0.69872	0.00035	-15.47	3
NIST612	31.8	78.4	1.181	0.70906	0.00002	1.205	0.004	2.02	0.70313	0.00126	-8.37	3
BCR-2G	47.0	342	0.400	0.70500	0.00001	0.402	0.020	0.50	0.70498	0.00029	-0.04	12
BHVO-2G	9.18	396	0.068	0.70347	0.00001	0.066	0.004	-1.99	0.70348	0.00026	0.01	30
TB-1G	142	1352	0.306	0.70558	0.00002	0.311	0.001	1.58	0.70551	0.00007	-0.10	3
NKT-1G	30.7	1195	0.075	0.70351	0.00002	0.073	0.000	-3.14	0.70357	0.00008	0.09	5
ATHO-G	65.3	94.1	2.021	0.70327	0.00002	2.080	0.238	2.89	0.68598	0.00460	-24.58	4
KL2-G	8.70	356	0.071	0.70357	0.00002	0.070	0.005	-2.08	0.70357	0.00021	0.01	7
ML3B-G	5.80	312	0.054	0.70385	0.00001	0.055	0.002	1.95	0.70377	0.00037	-0.11	11
StHs6/80-G	30.7	482	0.186	0.70354	0.00004	0.182	0.013	-2.01	0.70368	0.00027	0.20	6
T1-G	79.7	284	0.817	0.71014	0.00000	0.833	0.038	1.89	0.71007	0.00044	-0.10	28
YG4301	0.670	1058	0.002	0.70343	0.00002				0.70335	0.00016	-0.10	18
YY12-01	0.090	192	0.001	0.70358	0.00001				0.70349	0.00035	-0.12	8
HNB09	0.008	50.9	0.000	0.70374	0.00001				0.70368	0.00055	-0.08	10

* Rel. error (%) is relative error and = (measured value / reference value - 1) $\times$ 100; # Rel. error (%) = (measured value / reference value - 1) $\times$ 1000

ablation position with the aerosol extraction position. Helium gas was filled into the ablation cell, while argon was mixed into the sample-out line downstream from the ablation chamber before entering the torch. A signal-smoothing device was used downstream from the sample cell, which significantly reduced the short-term variability of the signal.²⁰ Details of the instrumental operating conditions and measurement parameters are summarized in Table 1.

Samples. The well-characterized reference materials (RMs) from the National Institute of Standards and Technology (NIST, USA) glasses (610 and 612), the United States Geological Survey (USGS) RMs (BCR-2G (basalt), BHVO-2G (basalt), NKT-1G (nephelinite), TB-1G (basalt)), and the Max Planck Institute (MPI-DING, Germany) glasses (ATHO-G (rhyolite), KL2-G (basalt), ML3B-G (basalt), StHs6/80-G (andesite), T1-G (quartz-diorite)) were used as the external standards for measurement of the $^{87}\text{Rb}/^{86}\text{Sr}$ ratio and as unknown samples for measurement of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio. Two natural clinopyroxenes (NHB and YY12-01) and one natural anorthite (YG4301) were used as the unknown samples to evaluate the data quality of $^{87}\text{Sr}/^{86}\text{Sr}$. The recommended values of the $^{87}\text{Rb}/^{86}\text{Sr}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for the RMs are listed in Table 2. The mass fractions of Sr and Rb and the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in the reference glasses are compiled from the literature.^{13, 21-28}

Two different lunar meteorites (NWA 10597 and NWA 6950) were analyzed for Rb-Sr isotopes. NWA 10597 is a low-Ti mare basaltic lunar meteorite and consists mostly of mm-sized pyroxene and plagioclase, with minor olivine, spinel, ilmenite, phosphates,

silica, and trace Zr-rich minerals, such as baddeleyite, zirconolite and tranquillityite. The *in situ* U-Pb analyses of baddeleyite and apatite using SIMS reveal a mutually consistent age of ~ 3.0 Ga.²⁹ ³⁰ NWA 6950 is a 224.5 g meteorite that was found in Morocco in 2000 and has been identified as a lunar olivine gabbro. NWA 6950 is mainly composed of olivine and pyroxene with minor plagioclase. Additionally, chromite, ilmenite, phosphate, baddeleyite, K-feldspar, troilite, and Fe-Ni metal occur as accessory phases. The *in situ* U-Pb dating of baddeleyite and phosphate in NWA 6950 implies two crystallization ages: 3187 ± 18 and 3120 ± 18 Ma.³¹

LA-MC-ICP-MS measurement and data reduction. Detailed analytical procedures for Sr isotopic composition are described by Zhang *et al.* (2018).¹³ In summary, the combination of high-sensitivity X-skimmer cone and JET-sample cone was employed, and the mass spectrometer was operated in low mass resolution mode. A small amount of N_2 (12 mL min^{-1}) was added to the carrier gas flow by using a simple Y connector behind the signal-smoothing device. NIST 610 was used to optimize the instrumental parameters, including the He and Ar gas flow rates, the torch position, the RF power setting, and the source lens settings for maximum sensitivity and optimum peak flatness. The routine data acquisition consisted of one block of 120 cycles (0.524 s integration time per cycle), with the first 30 cycles for background collection (no laser ablation) and the remaining 90 cycles for signal collection. Note that only 60-70 cycles were finally used to calculate the isotope ratios; the cycles at the beginning and at the end of the laser ablation were discarded. The samples were measured with different laser ablation parameters

Fig. 2 The repeated measurement results of $^{87}\text{Sr}/^{86}\text{Sr}$ in 14 reference materials by LA-MC-ICP-MS (a), and part of reference materials with $^{87}\text{Rb}/^{86}\text{Sr}$ lower than 1 (b). The red crosses represent the average values with uncertainty of 2SD. Gray circles represent the analytical results from individual runs.

Fig. 3 The relationship between ^{88}Sr signal intensity and the U_{SE} and U_{SD} of $^{87}\text{Sr}/^{86}\text{Sr}$ (a) and between ^{85}Rb signal intensity and the U_{SE} and U_{SD} of $^{87}\text{Rb}/^{86}\text{Sr}$ (b). Note that the U_{SE} and U_{SD} of $^{87}\text{Sr}/^{86}\text{Sr}$ are multiplied by 1000. The U_{SE} and U_{SD} of $^{87}\text{Rb}/^{86}\text{Sr}$ are relative values = $(U_{SE} \text{ or } U_{SD}) / \text{the average value}$. All data are from the 14 reference materials.

based on the Sr concentration in the samples. The detailed setup parameters of the laser system and the MC-ICP-MS are listed in Table 1. The data reduction for LA-MC-ICP-MS analysis was conducted with the ISO-Compass software.³² The interference correction strategy was the same as reported by Zhang et al. (2018).¹³ The regions of integration for both the gas background and the sample were selected first. Following background correction, which removes the background Kr^+ signals, no additional Kr peak stripping was applied. The interferences were corrected by using the following sequence: (a) the interferences of $^{168}\text{Er}^{++}$ on ^{84}Sr , $^{170}\text{Er}^{++}$ and $^{170}\text{Yb}^{++}$ on ^{85}Rb , $^{172}\text{Yb}^{++}$ on ^{86}Sr , and $^{174}\text{Yb}^{++}$ on ^{87}Sr were corrected based on the measured signal intensities of $^{167}\text{Er}^{++}$, $^{173}\text{Yb}^{++}$, $^{84, 86-88}\text{Sr}$ and ^{85}Rb and the natural isotope ratios of Er and Yb; (b) the isobaric interference of ^{87}Rb on ^{87}Sr was corrected by monitoring the ^{85}Rb signal intensity and a user-specified $^{87}\text{Rb}/^{85}\text{Rb}$ ratio using the exponential law for mass bias. The user-specified $^{87}\text{Rb}/^{85}\text{Rb}$ ratio was calculated by

measuring some reference materials with a known $^{87}\text{Sr}/^{86}\text{Sr}$ ratio. Following the interference corrections, mass fractionation of the Sr isotopes was corrected by assuming $^{88}\text{Sr}/^{86}\text{Sr} = 8.375209^{33}$ and applying the exponential law.³⁴

The $^{87}\text{Rb}/^{86}\text{Sr}$ ratio was calculated using the ^{85}Rb and ^{88}Sr signals and the $^{87}\text{Rb}/^{85}\text{Rb}$ of 0.385706 and $^{86}\text{Sr}/^{88}\text{Sr}$ of 0.119351. External calibration was used to correct the elemental fractionation between Rb and Sr. A series of reference glasses was analyzed to provide an average correction factor. Then the average factor was used for the samples and reference materials. This data reduction procedure was also employed using the ISO-Compass software.

Based on the LA-MC-ICP-MS method described above, $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{87}\text{Rb}/^{86}\text{Sr}$ in different glasses, clinopyroxenes and anorthite were measured to evaluate the data quality. Fig. 2 shows the relative error of $^{87}\text{Sr}/^{86}\text{Sr}$ in the reference materials (the relative

Fig. 4 The typical signal profiles of ^{88}Sr , ^{85}Rb and $^{87}\text{Rb}/^{86}\text{Sr}$ from the analyzed plagioclase (a) and glass (b) in lunar meteorites by LA-MC-ICP-MS.

error = (measured values / recommended value – 1) $\times$ 1000). When the $^{87}\text{Rb}/^{86}\text{Sr}$ ratio was higher than 1, such as for NIST 610 ($^{87}\text{Rb}/^{86}\text{Sr}$ = 2.332), NIST 612 ($^{87}\text{Rb}/^{86}\text{Sr}$ = 1.181) and ATHO-G ($^{87}\text{Rb}/^{86}\text{Sr}$ = 2.021), large relative errors of more than 10 % were obtained (Fig. 2a), implying that the Rb interference cannot be accurately corrected. For other reference materials with a $^{87}\text{Rb}/^{86}\text{Sr}$ ratio of less than 1, relative errors of less than 0.2 % were obtained, even when the Sr mass fractions were as low as 50 $\mu\text{g g}^{-1}$ (HNB-9, Fig 2b and Table 2).

The repeated results of $^{87}\text{Rb}/^{86}\text{Sr}$ in the reference materials are shown in Table 2. The relative errors ((measured values / recommended value – 1) $\times$ 100, %) in 11 glasses ranged from -3.46 % to 2.89 %, independent of the Sr or Rb mass fractions. Therefore, the accuracy of $^{87}\text{Rb}/^{86}\text{Sr}$ in this study was about 3 %.

The repeatability of $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{87}\text{Rb}/^{86}\text{Sr}$ in an individual run was assessed by the standard error (SE):

$$SD = \sqrt{\frac{\sum(X-\bar{x})^2}{n-1}} \quad (\text{Eq. 1})$$

$$SE = \frac{SD}{\sqrt{n}} \quad (\text{Eq. 2})$$

where SD is the standard deviation; X is the isotope ratio in each cycle, $\bar{x}$ is the mean value; n is the number of values in one individual run. Here, the SD and SE values with the confidence interval of 95% were called U_{SD} and U_{SE} , respectively. U_{SD} represents an estimate of the variability of the isotope ratios in one individual run. U_{SE} represents the variation of the average value in one individual run. As shown in Fig 3a, both U_{SD} and U_{SE} of $^{87}\text{Sr}/^{86}\text{Sr}$ depended on the signal intensity of ^{88}Sr . Therefore, we can estimate the precision of $^{87}\text{Sr}/^{86}\text{Sr}$ in unknown samples based on their signal intensity of ^{88}Sr and the regression lines from reference materials. The same rule can also be observed in the

relationship between U_{SD} and U_{SE} of $^{87}\text{Rb}/^{86}\text{Sr}$ and the signal intensity of ^{85}Rb (Fig. 3b).

Based on the results of accuracy and precision from the measurements of the 14 reference materials, we designed a reasonable technical criterion to filter the undesirable data during actual sample analyses.

(a) The data of the $^{87}\text{Rb}/^{86}\text{Sr}$ ratio of more than 1 should be deleted due to invalid correction of the Rb interference.

(b) The data of the ^{88}Sr signal of less than 0.2 V should be discarded due to the poor precision of $^{87}\text{Sr}/^{86}\text{Sr}$.

RESULTS AND DISCUSSION

The signal features of natural samples

In this study, several techniques were used to ensure that the Sr signal intensity is high enough for precise measurements, such as line scan mode with a scan speed of 2-6 $\mu\text{m s}^{-1}$, high ablation frequency with a laser pulse repetition rate of 10-30 Hz, and large spot size of 50-60 μm . The typical laser ablation craters are shown in Fig. S2. Two different types of signal profiles were observed during the analyses of the natural minerals in the meteorites. In the first type, the Sr and Rb signal profiles are stable, indicating the homogenous distribution of Sr and Rb in the ablated area (Fig. 4a). Then, high precision of $^{87}\text{Rb}/^{86}\text{Sr}$ can be obtained. By contrast, dramatic fluctuations of the Sr and Rb signals occurred in the second type during the laser ablation process, resulting in the obvious variation of $^{87}\text{Rb}/^{86}\text{Sr}$ by more than one order of magnitude (Fig. 4b). This phenomenon could be attributed to the heterogeneous distribution of the Sr and Rb concentrations. The obtained $^{87}\text{Rb}/^{86}\text{Sr}$ ratio is inaccurate and has poor precision when

Fig. 5 The plot of $^{87}\text{Rb}/^{86}\text{Sr}$ versus $^{87}\text{Sr}/^{86}\text{Sr}$ for the data from Fig. 4(b).

Fig. 6 The plot of $^{87}\text{Rb}/^{86}\text{Sr}$ versus $^{87}\text{Sr}/^{86}\text{Sr}$ for the data of the Normal group ($n = 36$) and the SUIA group ($n = 244$) in the NWA 10597.

Fig. 7 The results of Rb-Sr isochron age calculated by IsoplotR for the data of the Normal group and the SUIA group in the NWA 10597 (a, b).

normal data reduction was used to calculate the $^{87}\text{Rb}/^{86}\text{Sr}$ ratio. Unfortunately, in the analyses of the meteorites, the second signal profile type (Fig. 4b) appeared frequently in clinopyroxenes, ilmenites, and silicate glasses, which seriously affected the quality of $^{87}\text{Rb}/^{86}\text{Sr}$.

Here, we established a new data reduction strategy. The smallest unit of data stored in MC-ICP-MS was called cycle in an individual run. After the corrections of background, interference, mass fractionation of $^{87}\text{Sr}/^{86}\text{Sr}$, and the external standard of $^{87}\text{Rb}/^{86}\text{Sr}$ for each cycle, we can plot $^{87}\text{Rb}/^{86}\text{Sr}$ versus $^{87}\text{Sr}/^{86}\text{Sr}$ using all the cycles. For measurements with a large variation of the Sr and Rb signals, $^{87}\text{Rb}/^{86}\text{Sr}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ had a good correlation. Fig. 5 shows a typical plot of $^{87}\text{Rb}/^{86}\text{Sr}$ versus $^{87}\text{Sr}/^{86}\text{Sr}$ (data from Fig. 4b). According to the technical criterion described above, data with $^{87}\text{Rb}/^{86}\text{Sr}$ higher than 1 were deleted. Then the remaining data formed a regression line with a slope of 0.0451 and an intercept of 0.6997. The slope then can be used to calculate the Rb-Sr isochron age. Note that the data for each cycle do not have any uncertainty, which is unfavorable for calculating the isochron age. In order to resolve this problem, we assigned the uncertainties of $^{87}\text{Rb}/^{86}\text{Sr}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ in each cycle based on the signal intensities of ^{85}Rb and ^{88}Sr , respectively. The assignment criterion was based on the relationship between the uncertainties and the signal intensities obtained from the measurements in the 14 reference materials (Fig. 3). U_{SE} represents the variation of the average value and cannot show the variation range of each cycle during one individual run. Therefore, we selected the regression equation of U_{SD} versus signal intensity to estimate the uncertainty for each cycle. This data reduction method was called the smallest unit isochron age (SUIA).

Table 3 The calculation results of Rb-Sr isochron ages and initial $^{87}\text{Sr}/^{86}\text{Sr}$ by IsoplotR and Monte Carlo linear fitting for NWA 10597 and NWA 6950

Samples			Rb-Sr isochron age					Initial $^{87}\text{Sr}/^{86}\text{Sr}$			
			IsoplotR			Monte Carlo Linear Fitting	Uncertainty	IsoplotR		Monte Carlo Linear Fitting	Uncertainty
			Maximum likelihood	Uncertainty	MSWD			Maximum likelihood	Uncertainty		
NWA	Normal group	n=36	2929	33	24	2892	9	0.70036	0.00002	0.70033	0.00011
10597	SUIA group	n=244	2984	43	1.5	2995	9	0.70135	0.00031	0.70098	0.00060
NWA	Normal group	n=70	2507	33	21	2498	8	0.70380	0.00004	0.70352	0.00007
6950	SUIA group	n=986	3149	20	1.5	3153	11	0.70281	0.00008	0.70252	0.00012

Fig. 8 The plot of $^{87}\text{Rb}/^{86}\text{Sr}$ vs $^{87}\text{Sr}/^{86}\text{Sr}$ for the data of the Normal group (a) and the SUIA group (b) in the NWA 6950.

The Rb-Sr isochron age for meteorites

The minerals and glasses in the two meteorites were measured to determine the Rb-Sr isochron age. The normal data reduction and SUIA were used to process the different types of the signal profiles. Below we will introduce and discuss the isochron age results in the two meteorites.

NWA 10597. The plagioclases, pyroxenes, and ilmenites in NWA 10597 were measured randomly. Thirty-six individual runs showed stable Sr and Rb signal intensities, leading to good analytical precisions. Therefore, these data were processed using the normal correction method and called Normal group. At the plot of $^{87}\text{Rb}/^{86}\text{Sr}$ versus $^{87}\text{Sr}/^{86}\text{Sr}$ (Fig. 6), the regression line in the Normal group has a slope of 0.0413, an intercept of 0.7003 and a correlation coefficient of 0.9465 (R^2). On the other hand, six individual runs showed large variations of $^{87}\text{Rb}/^{86}\text{Sr}$, and were processed by the SUIA. In total, 244 cycles were obtained and called the SUIA group. As shown in Fig. 6, the SUIA group data also yielded a good regression line, with a slope of 0.0417, an intercept of 0.701 and a correlation coefficient of 0.9126 (R^2). The data of the Normal group and the SUIA group are listed in Table S1. IsoplotR was used to calculate the Rb-Sr isochron ages.³⁵ The Rb-Sr isochron age of the Normal group was 2928.5 ± 33.0 Ma (Fig. 7a), which is like the $^{207}\text{Pb}/^{206}\text{Pb}$ age of 3005 ± 5 Ma obtained

from baddeleyites and zirconolites and the $^{207}\text{Pb}/^{206}\text{Pb}$ age of 3031 ± 9 Ma obtained from apatites.²⁹ However, the MSWD of 24 was high, indicating the large dispersion in the Normal group's data, especially for the data with $^{87}\text{Rb}/^{86}\text{Sr}$ ranging from 0.05 to 0.15. These data generally were measured in pyroxenes. The Rb-Sr isochron age of the SUIA group was $2983.7.5 \pm 42.8$ Ma with a small MSWD of 1.5 (Fig. 7b). The result indicated that the assigned uncertainties of $^{87}\text{Rb}/^{86}\text{Sr}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ for each cycle were reasonable. In addition, the Monte Carlo method was used to fit the regression line (simulation of 10,000 times). The fitted slopes were used to calculate the Rb-Sr isochron age by using the isochron dating equation. The age results from the Monte Carlo linear fitting were 2892 ± 9 Ma and 2995 ± 9 Ma for the Normal group and the SUIA group, respectively (Table 3), which is consistent with those from IsoplotR. However, the age uncertainties from Monte Carlo linear fitting are obviously smaller than those from IsoplotR. In addition, IsoplotR and Monte Carlo linear fitting gave similar initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios.

NWA 6950. The plagioclases, pyroxenes, ilmenites, and glasses in NWA 6950 were measured. Ninety-four individual runs showed stable Sr and Rb signal intensities and were classified into the Normal group. Twenty-one individual runs were processed by the SUIA group. In both groups, two different regression lines were

Fig. 9 The results of Rb-Sr isochron age calculated by IsoplotR for the data of the Normal group and the SUIA group in the NWA 6950 (a, b).

observed (Fig. 8). For example, 70 data in the Normal group gave a regression line with a slope of 0.0355 and an intercept of 0.7035, but the other line from the remaining 24 data had a slope of 0.0341 and an intercept of 0.7076. The SUIA group also showed a similar feature, including a line (986 cycles) with a slope of 0.0458 and an intercept of 0.7025, and the other line (326 cycles) with a slope of 0.0437 and an intercept of 0.7072. Most of the data with high initial $^{87}\text{Sr}/^{86}\text{Sr}$ (0.7072–0.7076) were measurements obtained for the glasses and pyroxenes in or around the black veins (Fig. S1). They are interpreted to have been affected by later geological processes. Therefore, we only kept the data with the initial $^{87}\text{Sr}/^{86}\text{Sr}$ around 0.703 (0.7025–0.7035), and used IsoplotR and Monte Carlo linear fitting to calculate the Rb-Sr isochron age.

The data of the Normal group and the SUIA group are listed in Table S2. Fig. 9a and 9b show the IsoplotR results. The Rb-Sr isochron ages of the Normal group and the SUIA group were 2506.8 ± 32.9 Ma with MSWD of 21 and 3149.3 ± 20.2 Ma with MSWD of 1.5, respectively. The Rb-Sr isochron ages calculated by Monte Carlo linear fitting were 2498 ± 8 Ma and 3153 ± 11 Ma for the Normal group and the SUIA group, respectively. The Rb-Sr isochron age of the Normal group is obviously younger than that of the SUIA group and the U-Pb ages of 3187 ± 18 Ma and 3120 ± 18 Ma obtained from baddeleyite and phosphate by SIMS. The younger age in the Normal group is attributed to the narrow range of $^{87}\text{Rb}/^{86}\text{Sr}$, which is mainly from 0.01 to 0.1. We found that plagioclases and pyroxenes generally had low and stable $^{87}\text{Rb}/^{86}\text{Sr}$, while glasses and ilmenites had high and scattered $^{87}\text{Rb}/^{86}\text{Sr}$. Therefore, the Normal group was mainly made up of data with low $^{87}\text{Rb}/^{86}\text{Sr}$ ratios. By contrast, data in the SUIA group mainly had high $^{87}\text{Rb}/^{86}\text{Sr}$ ratios (up to 1) and provided better estimation of the Rb-Sr isochron age.

CONCLUSION

In this study, an *in situ* Rb-Sr dating method for different lunar meteorites using LA-MC-ICP-MS was established. Based on the analytical results from many reference materials, we suggested that the isobaric interference of ^{87}Rb on ^{87}Sr can be corrected by using the mathematical calculation for the sample if the $^{87}\text{Rb}/^{86}\text{Sr}$ is lower than 1. Under this prerequisite, the accuracy of $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{87}\text{Rb}/^{86}\text{Sr}$ in reference glasses, clinopyroxenes and anorthite was better than 0.2 ‰ and 3 ‰, respectively. A new data reduction of SUIA was developed to resolve the problem of the high variation of $^{87}\text{Rb}/^{86}\text{Sr}$ in natural samples. The smallest unit of data was corrected and summarized to calculate the isochron age. Using the new reduction method, the Rb-Sr isochron age of 2984 ± 43 Ma for NWA 10597 and 3149 ± 20 Ma for NWA 6950 was determined. The age results are like the U-Pb dating ages (2990–3032 Ma for NWA 10597 and 3210–3187 Ma for NWA 6950) obtained for baddeleyite and apatite by using SIMS. The analytical results suggest that the *in situ* Rb-Sr dating method presented in this study can be used to determine the age of lunar meteorites. Compared to the small and rare baddeleyites and apatites in meteorites, the targets for *in situ* Rb-Sr dating can be the main component phases of different planetary materials.

Compared to ICP-MS/MS (such as with the Agilent 8800) or MC-ICP-MS with collision cell, the present method cannot measure $^{87}\text{Sr}/^{86}\text{Sr}$ in the Rb-rich sample with an $^{87}\text{Rb}/^{86}\text{Sr}$ ratio > 1, which limits the application for young geological samples. However, when the main constituent phases (plagioclase, pyroxene, and glass) in old meteorites are targeted and measured, the present method provides higher analytical precision and

accuracy for $^{87}\text{Sr}/^{86}\text{Sr}$ isotope analysis as compared with ICP-MS/MS analysis. The MC-ICP-MS instrument with collision cell can resolve the interference of ^{87}Rb and provides excellent $^{87}\text{Sr}/^{86}\text{Sr}$ data. However, it is a new mass spectrometry system, very expensive, and thus increases the cost of analysis. Its popularity is still low in the global market.

ASSOCIATED CONTENT

The supporting information (Figs S1-S2; Tables S1-S2) is available at www.at-spectrosc.com/as/home

AUTHOR INFORMATION

Wen Zhang is an associate professor at State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences, Wuhan. He received the doctor of geochemistry degree from China University of Geosciences (Wuhan) in 2015. His research interests primarily focus on: 1) the *in situ* isotope ratio analysis using LA-MC-ICP-MS, such as S-Cu-Fe-Zr-Sr-Nd-Hf-Pb, 2) the development of the preparation process for quantitative analysis of major and trace elements, 3) the synthesis reference materials for elements and isotope ratios analysis using LA-ICP-MS. He has published over 60 peer-reviewed scientific papers in ISI-indexed journals, including *Analytical Chemistry*, *Atomic Spectroscopy*, *Chemical Geology*, *Geostandards and Geoanalytical Research*, *Analytica Chimica Acta*, and *Journal of Analytical Atomic Spectrometry*.

Corresponding Author

*W. Zhang

Email address: tuyaken@hotmail.com

Notes

The authors declare no competing financial interest.

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