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The advent of double-Wien filter-selection-aperture and hexapole-collision-cell technologies coupled to laser ablation multicollector inductively coupled plasma mass spectrometry (LA-MC-ICP-MS/MS) enables in situ analysis of 87 Sr variations produced by the decay of radioactive 87 Rb ($t_{1/2} = 49.61 \pm 0.16$ Ga). We present methodologies to acquire *in situ* ⁸⁷Rb−⁸⁷Sr data using a Thermo Scientific™ Neoma™ MC-ICP-MS coupled to a laser ablation system. The ions first pass through a mass filter that blocks ions outside of the Rb-Sr mass region. The ions then travel through a hexapole collision cell filled with SF₆, inducing the fluorination of Sr⁺ to form SrF⁺. Strontium isotopes are measured as SrF⁺ free of interferences, while rubidium isotopes are measured as Rb⁺. Formulas are presented to calculate the error ellipses of ⁸⁷Rb/⁸⁶Sr and ⁸⁷Sr/⁸⁶Sr ratios corrected for instrumental fractionation by standard bracketing. While LA-MC-ICP-MS/MS is not as precise as Thermal Ionization Mass Spectrometry (TIMS), it is less destructive and sample throughput is higher. It is therefore particularly well suited to analyze small and precious samples, or to examine population characteristics. We have analyzed several terrestrial and extraterrestrial materials to showcase the unique capabilities of LA-MC-ICP-MS/MS in Sr isotopic analyses: (1) an orthoclase megacryst and other minerals from the 397 Ma Shap granite, (2) feldspar grains from the 26.5 ka Oruanui supereruption in New Zealand, (3) Durango apatite, (4) highly refractory hibonite inclusions from the Murchison meteorite, and (5) the martian meteorite NWA 7034 also known as Black Beauty. Black Beauty is a polymict breccia that contains zircons as old as 4.4 Ga but whose ⁴⁰Ar/³⁹Ar age was partially reset at 1.4 Ga. All K-feldspar grains analyzed in Black Beauty give an 87 Rb 87 Sr age of 2.189 \pm 0.059 Ga. Most likely, the 2.2 Ga 87 Rb $^{-87}$ Sr age represents the age of lithification. This study demonstrates the great potential of *in situ* ⁸⁷Rb-⁸⁷Sr dating for analyzing samples returned by planetary exploration missions, such as those currently collected by the Perseverance rover on Mars, or those that will be returned from Phobos by the MMX mission.

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[†] Electronic supplementary information (ESI) available: Mathematica program for reduction of Rb–Sr laser ablation data (LASr). Excel spreadsheet containing all the laser ablation data reported here. Supplementary Fig. S1. See https://doi.org/10.1039/d2ja00135g

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1. Introduction

Rubidium is a monovalent alkali metal that chemically very closely follows potassium, while strontium is a divalent alkaline-earth metal more similar to other group II elements like calcium. Many of the processes that have shaped planetary bodies have fractionated Rb from Sr, which over time produced variations in the ⁸⁷Sr/⁸⁶Sr ratio from the decay of radioactive 87 Rb ($t_{1/2} = 49.61 \pm 0.16$ Ga^{1,2}). The more straightforward application of ⁸⁷Rb-⁸⁷Sr systematics is dating of rocks,³ but this system has found applications in very diverse fields, covering for example: (1) the history of continental crust extraction and emergence, oceanic crust recycling, mantle mixing, and the nature of Hadean crust,⁴⁻⁹ (2) magma mixing and assimilation of country rocks,¹⁰⁻¹⁵ (3) the timing of depletion in moderately volatile elements in Earth, the Moon, and other planetary bodies,^{16–18} (4) correlation between rock strata during periods of Earth's history that saw rapid changes in the Sr isotopic composition of seawater,19,20 (5) animal and hominid origin and migration,²¹⁻²⁷ and (6) past exchanges of cultural artifacts and commercial goods between different regions.²⁸⁻³⁰ The materials targeted in those studies are diverse and comprise K-rich minerals such as alkali feldspars and micas, bulk silicate and carbonate rocks, phosphates of igneous and biological origins, surface and underground water, and man-made materials.

Strontium isotopic analysis can be readily done by thermal ionization mass spectrometry (TIMS) as Sr is efficiently ionized using this technique (ref. 31 and references therein). Such measurements, however, are not always possible when high Rb/ Sr grains are too small to be separated. When such measurements are possible, they still require sampling, digestion, Sr purification by chromatography in a clean laboratory setting, Sr loading on a filament, and analysis by TIMS. In situ Sr isotopic analysis can expand the range of applicability of ⁸⁷Rb-⁸⁷Sr studies to new targets and provide a higher sample throughput, whilst minimizing sample destruction of precious samples such as human remains, meteoritic samples, or cultural artifacts. The difficulty of such measurements lies, however, in the presence of isobaric interferences on Sr isotopes, in particular 87 Rb on 87 Sr which requires a mass resolving power of about 3 imes10⁵ to effectively separate. Strategies have been developed to minimize these interferences, the most notable being (1) focusing on low Rb samples such as carbonate, apatite or plagioclase and correcting for possible isobaric interferences via measurement of the ⁸⁵Rb and peak-stripping assuming a constant value for ⁸⁵Rb/⁸⁷Rb,³²⁻³⁹ (2) using resonant ionization mass spectrometry (RIMS) to only ionize Sr by using lasers with wavelengths tuned to a specific electronic transition of Sr such that Rb is not ionized,^{4,40-43} and (3) using a reactive gas such as N_2O , O_2 , CH_3F , or SF_6 in a collision/reaction cell (CRC) to react Sr⁺ but not Rb⁺, with the former analyzed as molecular ions SrO⁺ or SrF⁺.44-53

The latter approach often involves the use of a pre-cell quadrupole mass filter to remove the ions in the mass range that would otherwise interfere with molecular Sr ions (*e.g.*, 106 Cd⁺ interfering with 87 Sr¹⁹F⁺). Such measurements are

usually performed on a single collector ICP-MS, which has limited precision due to inherent changes in beam intensity of transient laser ablation signals. A prototype instrument named Proteus was developed that combines a quadrupole mass-filter and collision/reaction cell with a MC-ICP-MS, permitting the measurement of all Sr isotopes in multicollection.⁵¹ The precision of Sr isotopic analyses was improved compared to single collector mass spectrometers and demonstration was made that this approach could be used for in situ ⁸⁷Rb-⁸⁷Sr dating of geological materials. The design of Proteus, however, suffered from low sensitivity compared to other MC-ICP-MS and the fact that instrumental mass bias did not follow mass-dependent fractionation, rendering accurate corrections problematic. More recently, another prototype instrument was developed called Vienna that addressed the shortcomings of Proteus.52 It relied on a novel mass-filter and collision/reaction cell module that has now been implemented on the commercially available Neoma MC-ICP-MS from Thermo Fisher Scientific™. The Vienna MC-ICP-MS/MS was built around an earlier generation Thermo Scientific[™] Neptune[™] MC-ICP-MS while the Neoma MS/MS is based on a new, more sensitive, user-friendly, and electronically stable MC-ICP-MS platform. Both Vienna and the Neoma MS/MS use (1) a double Wien filter separated by an adjustable aperture for mass selection and (2) a hexapole collision/reaction cell. The operation of the Neoma MS/MS as applied to in situ Sr isotopic analyses is detailed in Sect. 2. While the Vienna and Neoma MS/MS rely on the same technology, the hardware and software of the two instruments differ. Both Proteus⁵¹ and Vienna⁵² were prototype instruments that paved the way for the development of the commercially available Neoma MS/MS. We report here tests of in situ Sr analyses with the Neoma MS/MS coupled to a 193 nm excimer laser ablation system. All laser ablation data reported below are compiled in a .xlsx file provided as ESI.†

2. Materials and methods

Laser ablation was performed using a NWR193-UC 193 nm excimer laser ablation system (ESI Lasers). The mass spectrometer used was a precommercial version of the Thermo Scientific Neoma MC-ICP-MS with MS/MS option (Fig. 1) operated under the Qtegra ISDS[™] software (v2.12). Below, we start with a description of the Neoma MS/MS hardware, with focus on the double Wien filter-hexapole collision cell as applied to Sr isotopic analyses.⁵² We then give details on the measurement conditions. Finally, we explain how the data reduction was done, including handling of transient laser ablation data with a Mathematica-based software (LASr) and error propagation.

2.1. Prefilter and collision/reaction cell technology

The Neoma MS/MS uses the same ICP technology as the Thermo ScientificTM iCAPTM Qnova series of ICP-MS and ICP-OES instruments. The interface between the ICP and the mass spectrometer is an update of the Jet Interface, first introduced on the Thermo ScientificTM Neptune PlusTM MC-ICP-MS. After acceleration by an extraction voltage of -2 kV, the ions enter



Fig. 1 Simplified schematics of the Neoma MC-ICP-MS/MS. After ionization in the plasma (1), the ions are accelerated by an extraction voltage (2). They then enter a first Wien filter (3). The opposite magnetic and electric forces are balanced when the entrance velocity is v = E/B. The ratio *E/B* is adjusted to let ions in the mass region of Sr pass. Heavier (e.g., Cd⁺) and lighter (e.g., Ar⁺) ions enter the Wien filter with lower and higher velocities than Sr and are deflected, resulting in their collision with an adjustable slit aperture (4). This slit aperture effectively acts as a mass filter. The ions that pass through the slit then go through an inversion lens (5) and are recollimated using a second Wien filter (6). The Sr⁺ and Rb⁺ ions then pass through a hexapole collision/reaction cell where SF₆ is injected (7). Sr⁺ ions readily react with SF₆ to make SrF⁺ while Rb⁺ ions do not react. Rb⁺ and SrF⁺ then pass through an electrostatic analyzer (8), which is part of the double-focusing geometry to compensate for the spread in ion velocities generated by the plasma source. The ions are then separated according to their mass-to-charge *m/q* ratio in a magnetic sector (9). The separated ion intensities are measured on Faraday collectors (10), with ⁸⁵Rb and ⁸⁷Rb measured at *m/q* = 85 and 87, while ⁸⁶Sr, ⁸⁷Sr, and ⁸⁸Sr are measured as fluorides at *m/q* = 105, 106, and 107, respectively.

a novel ion optics Prefilter module composed primarily of two Wien filters separated by an inversion lens and adjustable aperture. The Wien velocity filter/mass spectrograph was developed in 1898 and provided the first hint for the existence of the proton,⁵⁴ which was later discovered by Ernest Rutherford. This filter consists of near-uniform orthogonal magnetic (intensity B_w) and electrostatic (intensity E_w) fields that pull charged particles in opposite directions. Putting aside the dispersion in energy and velocity of ions in the plasma source, the ions accelerated by the extraction voltage enter the first Wien filter with a velocity $v = \sqrt{2qU/m}$, where q is the charge $(1.6 \times 10^{-19} \text{ C for singly charged ions})$, U is the acceleration voltage (-2000 V), and *m* is the isotopic mass $(1.4 \times 10^{-25} \text{ kg for})$ 87 Sr). The electrostatic force in the Wien filter is qE_{w} , while the magnetic force is qvB_w . When the magnetic and electrostatic forces are balanced ($E_w = \nu B_w$), the ion trajectory remains undisturbed, which happens for ions of mass-to-charge ratio m/ $q = 2U(B_w/E_w)^2$. Ions with a different mass-to-charge ratio will fan out and collide with the adjustable aperture that separates the two Wien filters. By adjusting the ratio of B_w/E_w in the first Wien filter and the aperture opening, it is thus possible to permit the transmission of ions within a certain mass range. Those that pass through the aperture are bent back towards the central axis by the inversion lens and are recollimated using the second Wien filter (the values of B_w and E_w are the same as the first Wien filter). For Rb–Sr isotopic analyses, the ratio B_w/E_w and the aperture are adjusted to remove Ar⁺ and all atomic and molecular ion interferences in the SrF⁺ mass region (Fig. 1).

After exiting the Prefilter, the ions enter a hexapole CRC where SF_6 is injected. Collisions with gaseous SF_6 induce some scatter and the role of the hexapole is to keep the ions focused.

Upon colliding with the gas, almost all (>85%) strontium is fluorinated to make SrF⁺ ions, while rubidium remains as Rb⁺.⁴⁹ Fluorine has only one stable isotope ¹⁹F, therefore the proportions of SrF⁺ ion isotopologues are those of Sr isotopes. The ions then pass through a standard double-focusing geometry electrostatic analyzer (ESA) and magnetic sector, where they are separated according to their mass-to-charge ratios. The ion intensities are measured in Faraday collectors. The Neoma MS/ MS is equipped with 11 Faraday collectors that can all be connected to amplifiers with 10¹³, 10¹¹, and 10¹⁰ Ω feedback resistors. Deflection plates in front of the axial Faraday can deflect the signal to a discrete dynode secondary electron multiplier (not used in this study).

The Prefilter removes atomic and molecular ions outside of the Rb–Sr mass region. The CRC fluorinates Sr through the ion– molecule reaction $Sr^+ + SF_6 \rightarrow SrF^+ + SF_5$, while Rb remains unchanged. The Prefilter and CRC module enable precise and accurate *in situ* ⁸⁷Sr/⁸⁶Sr ratio analyses in Rb-rich samples by measuring Sr isotopes as SrF⁺ at a mass where interferences have been eliminated by the Prefilter.^{51,52}

2.2. Measurement conditions

The mass spectrometer and laser ablation system were controlled using the Qtegra ISDS and ActiveView2 software, respectively. The laser ablation system had a TwoVol2 two-volume laser ablation cell that was flushed with 1200 mL min⁻¹ He. N₂ was added after the ablation cell at a rate of 4 mL min⁻¹. All measurements were made with a 100 μ m spot size, laser fluence of 5 J cm⁻², with a repetition rate of 20 Hz, unless stated. We used two laser ablation/data acquisition

schemes depending on whether Sr isotopic analysis was the sole focus, or Rb/Sr ratio measurements were also needed (Sr-only and Rb + Sr hereafter). For Sr-only measurements, the data were acquired over 2 minutes comprising 120 measurement cycles of 1 s each. Laser ablation lasted for 60 s. Data acquisition was started 30 seconds prior to ablation and measurable signal was sustained for \sim 45 s. The maximum signal achieved on SRM@610 (Sr = 515.5 ppm) at the beginning of the ablation was $\sim 4.7 \times 10^7$ cps on ${}^{88}\text{Sr}{}^{19}\text{F}^+$. We give all ion intensities in cps, which can easily be converted to a voltage measured on a $10^{11} \Omega$ amplifier by dividing by 6.24×10^7 (4.7×10^7 cps corresponds to ~ 0.75 V). The intensity of the transient signal on SRM610 decayed from the maximum by a factor of \sim 0.97 per second of ablation. The Rb + Sr analyses were performed in peak jumping mode. An issue in the precommercial instrument software prevented us from reducing the settling time between peak jumps below 3 s, which is the value that we used (a 0.5 s settling time would have been sufficient to accommodate the response time of the $10^{11} \Omega$ amplifiers⁵¹). The Rb + Sr measurements consisted of 20 cycle measurements in a sequence 2 s Sr-3s

settling time-0.5 s Rb-3s settling time. The arrival and departure times of Rb⁺ and SrF⁺ ion signals are the same as those in the Sr-only acquisition scheme.

All instrument conditions are tabulated in Table 1. The cooling and intermediate Ar gas flows were set at 14 and 0.8 L min⁻¹, respectively. The plasma power was set at 1200 W. The z-distance was fixed to 6.5 mm. Previous studies have shown that it can be advantageous to increase the distance between the sampler cone and the torch to reduce instrumental fractionation between Rb and Sr.^{51,55} Because this is done at the expense of sensitivity and our acquisition time was already penalized by a long settling time, we decided against that option and the torch position was tuned for sensitivity. Nickel Jet sampler and X skimmer cones were used. The three adjustable parameters for the Prefilter module are B_w/E_w which defines the passthrough mass, B_w which influences how ions of different mass-to-charge ratios fan out in the Wien filter, and the opening of the aperture separating the two Wien filters. The B_w/E_w ratio was adjusted to let Sr⁺ and Rb⁺ ions through, the magnetic field was then adjusted with the aperture partially closed to trim ions

Parameter	Value	Unit	Parameter	Value	Unit			
ESI Apex Omega Q desolvating	nebulizer system		ESI NWR193 UC laser ablation system with TwoVol2 cell					
Argon	3.8	$L \min^{-1}$	Helium	1.2	$L \min^{-1}$			
Nitrogen	3	$\rm mL~min^{-1}$	Nitrogen	4	$mL min^{-1}$			
Spray chamber	140	$^{\circ}\mathbf{C}$	Spot size	100	μm			
Peltier	3	$^{\circ}\mathrm{C}$	Fluence	5	$J \text{ cm}^{-2}$			
Desolvator	155	$^{\circ}\mathbf{C}$	Repetition rate	20	Hz			
Peripump	17	rpm	Dwell time	60	S			
Thermo Scientific Neoma MC-I	CP-MS with MS/M	S option	Thermo Scientific Neoma MC-ICP-MS with MS/MS option					
Cool gas flow	14	$L \min^{-1}$	Cool gas flow	14	L min ⁻¹			
Auxiliary gas flow	0.8	$L \min^{-1}$	Auxiliary gas flow	0.8	$L \min^{-1}$			
Nebulizer gas flow	0.9	$L \min^{-1}$	Nebulizer gas flow	0.89	$L min^{-1}$			
Torch horizontal position	-1.4	mm	Torch horizontal position	-1.35	mm			
Torch vertical position	-1.05	mm	Torch vertical position	-0.95	mm			
Sampling depth	5	mm	Sampling depth	6.5	mm			
Plasma power	1200	W	Plasma power	1200	W			
Resolving power	2100	MRP	Resolving power	2100	MRP			
Focus	52	%	Focus	52	%			
X Deflection	-14.8	%	X Deflection	-14.8	%			
Y Deflection	-3	%	Y Deflection	-3	%			
Shape	46.4	%	Shape	46.4	%			
Wien filter magnetic field	50	%	Wien filter magnetic field	50	%			
Wien filter electric field	320	V	Wien filter electric field	320	V			
Wien focus 1	-440	V	Wien focus 1	-440	V			
Wien focus 1 X symmetry	0	V	Wien focus 1 X symmetry	0	V			
Wien focus 1 Y symmetry	15	V	Wien focus 1 Y symmetry	15	V			
Slit angle	60	0	Slit angle	60	0			
Wien focus 2	-395	V	Wien focus 2	-395	V			
Wien focus 3	-370	V	Wien focus 3	-370	V			
Wien focus 3 X symmetry	0	V	Wien focus 3 X symmetry	0	V			
Wien focus 3 Y symmetry	-13	V	Wien focus 3 Y symmetry	-13	V			
CCT entry	-50	V	CCT entry	-50	V			
CCT bias	0	V	CCT bias	0	V			
CCT RF amplitude	100	%	CCT RF amplitude	100	%			
CCT exit 1	-85	V	CCT exit 1	-85	V			
CCT exit 2	-100	V	CCT exit 2	-100	V			
CCT SF ₆	36	$\mu L \min^{-1}$	CCT SF ₆	36	$\mu L \min^{-1}$			



Fig. 2 Illustration of mass window selection for *in situ* Sr isotopic analysis using the Prefilter and CRC of the Neoma MS/MS.⁵² The left panel shows the mass spectrum of a tune solution with the aperture wide open and the magnetic field of the prefilter set at 0.06T and the aperture opened (even in pass-through mode, the Prefilter magnetic field is set to a non-zero value to allow ion transmission). The right panel shows the same mass scan after the Prefilter is tuned to allow ions between mass 82 and 94 to pass (magnetic field of 0.315T and aperture closed to 60%). The same solution was used but interferences in the mass range of SrF⁺ (*e.g.*, Ag⁺) were removed by the MS/MS module. After reaction with SF₆ >85% of Sr is transmitted to the ESA-magnetic sector as Sr¹⁹F⁺ for isotopic analysis.

with m/q ratios lower or higher than Sr^+ and Rb^+ , and the aperture was finally adjusted to close the mass window more finely without encroaching on Sr⁺ and Rb⁺ masses. The Prefilter parameters used were $B_w/E_w = 0.030$, $B_w = 0.315T$ (B_w setting of 50%; 100% magnetic field strength corresponds to 0.63T) and the aperture 60% closed. Adjustment of these parameters was done by scanning ion masses with the magnetic field of the magnetic sector. Peak scans of a multielement solution containing Rb, Sr, Rh, Ag and many other elements are shown in Fig. 2 with the Prefilter set to full transmission without SF₆ in the CRC (left panel) and with the Prefilter closed to the mass range 82-94 with SF₆ injected in the CRC (right panel; this corresponds to the operating conditions under which we measured Sr isotopic ratios). As shown, Sr isotopes can be measured as SrF⁺ where isobaric interferences have been removed by mass selection in the Prefilter.

After passage through the Prefilter, the ions pass through the CRC. The flow rate of SF₆ in the collision cell was set to ~0.05 mL min⁻¹ (after conversion from the measured value of 0.2 mL min⁻¹ on a H₂ mass flow controller). Due to the low amount of SF₆ gas required, a gas mix of SF₆ in He⁵¹ would be preferred for this application. The conditions of the collision/reaction cell were tuned for maximum sensitivity on SrF⁺. When switching from Sr⁺ to SrF⁺ measurement conditions, the sensitivity decreased by 45%. The ions then pass through the ESA and the magnetic sector. Two acquisition schemes were used depending on whether both Rb and Sr were analyzed, or only Sr was measured (Table 2). In the Sr-only configuration, we set the magnetic field of the magnetic sector to measure ⁸³Kr¹⁹F⁺,

 $^{84}\text{Sr}^{19}\text{F}^+,\,^{85}\text{Rb}^{19}\text{F}^+,\,^{86}\text{Sr}^{19}\text{F}^+,\,^{87}\text{Sr}^{19}\text{F}^+$, and $^{88}\text{Sr}^{19}\text{F}^+$ on L3, L2, L1, C, H1, and H2. In the Rb + Sr configuration, we measured SrF⁺ using the same collector array, but a line was added to the sequence to measure $^{85}\text{Rb}^+,\,^{86}\text{Sr}^+,\,^{87}\text{Sr}^+$, and $^{88}\text{Sr}^+$ on L3, L2, L1, and C *via* peak jumping. All Faraday collectors were connected to 10^{11} \Omega amplifiers. These amplifiers saturate at 100 V (6.24 \times 10⁹ cps). The reason why we had to do Rb–Sr analyses in peak jumping mode is that on the precommercial instrument available, the outermost Faraday collectors were not properly positioned to allow simultaneous measurement of Rb⁺ and SrF⁺ ions in static mode.

The mass spectrometer was tuned first using a multielement solution and an Apex Omega Q desolvating nebulizer. The mass spectrometer was tuned again before each laser ablation sequence by running spot analyses on the SRM610 glass standard. With a flow rate of 100 μ L min⁻¹, using a 20 ppb Sr solution, we obtained ~9.4 × 10⁸ cps (~15 V) on ⁸⁸Sr¹⁹F⁺, which corresponds to a sensitivity of 700 V ppm⁻¹ and a useful yield for Sr of ~0.0025 ion at the collector per Sr atom injected (~0.25%). Overall, the Neoma MS/MS has similar sensitivity to the Neptune Series MC-ICP-MS in dry plasma conditions (using a desolvating nebulizer or laser ablation system) and is a factor of ~2 more sensitive than the Neptune in wet plasma conditions.

2.3. Data reduction and error propagation with LASr

Laser ablation data were exported from the Qtegra ISDS software as *xml* files that were then converted to *xlsx* files. The first step in the data reduction involved the use a *Mathematica*-based

Table 2 Cup configuration													
	L5	L4	L3	L2	L1	С	H1	H2	H3	H4	H5		
Rb			⁸⁵ Rb	⁸⁶ Sr	⁸⁷ Rb	⁸⁸ Sr	⁸⁹ Y	⁹⁰ Zr					
SrF			⁸³ KrF	⁸⁴ SrF	⁸⁵ RbF	⁸⁶ SrF	⁸⁷ SrF	⁸⁸ SrF					
Amplifier assignmer	nt		$10^{11} \Omega$	$10^{11} \ \Omega$	$10^{11} \ \Omega$	$10^{11} \ \Omega$	$10^{11} \ \Omega$	$10^{11} \Omega$					





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JAAS

Fig. 3 LASr Mathematica software for reduction of ⁸⁷Rb–⁸⁷Sr LA-MC-ICP-MS/MS data. The GUI software imports LA-MC-ICP-MS/MS data generated from Qtegra as an .xlsx file and exports another .xlsx file that contains the reduced data for each sample. (A) The user selects the reduction scheme to handle the transient laser ablation signal (average counts = average cps in the acquisition window; extrapolation to time zero = extrapolation of the data in the acquisition window to the start of the acquisition window; peak integration = the interpolated cps are integrated over the acquisition window). (B) Using dropdown menus, the user selects the lines where sample index, timestamp, label, and ion intensities are. (C) The user defines the entries that correspond to the table header. (D) Definition of the "blank" and "acquisition" windows. Sliders allow the user to move the three vertical lines in the bottom figure (red = l_1 , left blue = l_2 , right blue = l_3). Everything that is at the left of the red vertical line is used to define the blank (blank window), which is subtracted from the signal. The two blue vertical bars bracket the transient sample signal (acquisition window), which is used to calculate ⁸⁷Rb/⁸⁶Sr and ⁸⁷Sr/⁸⁶Sr ratios after blank subtraction. The actions taken in (D) are repeated for each laser analysis.

software called LASr (Fig. 3 and ESI[†]). Note that this is a purpose-developed program that we plan to continue developing in the future. The software uses a graphical user interface (GUI) that takes the user through several steps. First, a file is selected in a GUI file/directory navigator, after which the user selects which approach is used for handling the transient LA signal. Three options are available: (i) "Average counts", which uses the average counts for all isotopes in the acquisition window. (ii) "Peak integration", which involves integrating the signal over a user-set acquisition window, where the signal is linearly interpolated between adjacent data points (or linearly extrapolated if the boundary of the acquisition window does not coincide with a data point). This is the method that we adopted in our data reduction as Rb and Sr were measured in peak jumping mode and the integration method minimizes bias associated with spectral skew. (iii) "Extrapolation to time zero" extrapolates the data to the start of the acquisition window. The user then chooses, using dropdown menus, the entries in the

data table where the header entries are located for index, timestamp, and label, together with ion intensities for Rb, Sr, RbF, and SrF. For Sr-only measurements, the ion masses that need to be selected are ⁸⁴SrF, ⁸⁵RbF, ⁸⁶SrF, ⁸⁷SrF + ⁸⁷RbF, and ⁸⁸SrF. For Rb + Sr measurements, the same ion masses are selected, together with ⁸⁵Rb, ⁸⁷Rb + ⁸⁷Sr, and ⁸⁸Sr. The user then proceeds to another GUI window where the column header is selected, which will be trimmed during data reduction. The next step in the data reduction involves sequentially examining the intensity vs. time profile for each sample to define with a slider menu the time l_1 immediately before the signal starts rising, time l₂ when the laser ablation signal reaches its maximum, and time l_3 when the signal drops precipitously at the end of ablation. The program takes the average count-per-second signal in the *blank* time interval 0 to l_1 and subtracts it from the signal in the *acquisition* window l_2 to l_3 . The signal in the intervals $l_1 - l_2$ and l_3 -end is not used for any purpose.

Paper

The program then proceeds to calculate raw ${}^{87}\text{Rb}^+/{}^{86}\text{Sr}^+$ and internally normalized ${}^{87}\text{Sr}^+/{}^{86}\text{Sr}^+$ ratios using data in the acquisition window that have been blank-subtracted. Here, raw refers to ion ratios that have not been fully corrected for instrumental fractionation. This correction is done *via* standard bracketing and is discussed further below. The program first removes known isobaric interferences. No significant ${}^{83}\text{Kr}^{19}\text{F}^+$ was observed and no correction to subtract ${}^{84}\text{Kr}^{19}\text{F}^+$ and ${}^{86}\text{Kr}^{19}\text{F}^+$ from ${}^{84}\text{Sr}^{19}\text{F}^+$ and ${}^{86}\text{Sr}^{19}\text{F}^+$ was applied. The corrected interferences are from ${}^{87}\text{Rb}^{19}\text{F}^+$ on ${}^{87}\text{Sr}^{19}\text{F}^+$, and from ${}^{87}\text{Sr}^+$ on ${}^{87}\text{Rb}^+$. The later correction was used as a check that the ${}^{87}\text{Rb}^+/{}^{85}\text{Rb}^+$ ratio corresponded to the expected isotopic ratio for Rb, meaning that ${}^{85}\text{Rb}^+$ does not suffer from additional interferences. The raw ${}^{87}\text{Rb}^+/{}^{86}\text{Sr}^+$ ratio was simply calculated from the raw ${}^{85}\text{Rb}^+/{}^{86}\text{Sr}^{19}\text{F}^+$ ratio using the formula,

$$\frac{{}^{87}\text{Rb}^{+}}{{}^{86}\text{Sr}^{+}} = \frac{0.278346}{0.721654} \frac{{}^{85}\text{Rb}^{+}}{{}^{87}\text{Sr}^{19}\text{F}^{+}},$$
(1)

where the factor 0.278346/0.721654 corresponds to the ${}^{87}\text{Rb}/{}^{85}\text{Rb}$ ratio recommended by the IUPAC.⁵⁶ Instrumental and natural isotopic mass bias is assumed to follow the exponential law, which can be written as $a_2/a_1 = (A_2/A_1)(m_2/m_1)^{\beta}$ with a_2/a_1 the measured (fractionated) isotopic ratio, A_2/A_1 the true (reference) isotopic ratio, m_2/m_1 the ratio of isotopic masses, and β the coefficient of natural and instrumental mass bias. The coefficient of natural and instrumental mass bias is calculated using the interference-free ${}^{88}\text{Sr}/{}^{86}\text{Sr}$ ratio,

$$\beta_{\rm Sr} = \ln\left(\frac{\frac{^{88}{\rm Sr}^{19}{\rm F}^+ / {}^{86}{\rm Sr}^{19}{\rm F}^+}{8.37861}\right) / \ln\left(\frac{87.90561226}{85.90926073}\right), \qquad (2)$$

where 8.375209 is the 88Sr/86Sr ratio conventionally used for internal normalization of Sr isotopic ratios. This value was measured by Nier in 1938 in Sr metal57 and differs from the value of 8.37861 measured in the SRM987 carbonate standard.58 Because we use standard bracketing, the value of the ⁸⁸Sr/⁸⁶Sr ratio used for internal normalization has no consequence for the final value of the ⁸⁷Sr/⁸⁶Sr ratio that we report. Eqn (2) implicitly assumes that the isotopic fractionation acted on Sr isotopes rather than SrF isotopologues, as the masses used are those of Sr rather than SrF. This is a reasonable assumption to make because the coefficient of mass bias is dominated by instrumental fractionation (natural isotopic variations are small for Sr; $\sim \pm 0.3\%$ on the ⁸⁸Sr/⁸⁶Sr ratio⁵⁹) and much of the isotopic fractionation in MC-ICP-MS takes place in the torch-cone interface. We use this coefficient of mass bias to calculate (i) a fractionated ⁸⁷RbF⁺/⁸⁵RbF⁺ ratio used to subtract the ⁸⁷RbF⁺ interference on ⁸⁷SrF⁺, and (ii) correct the ⁸⁷SrF⁺/⁸⁶SrF⁺ ratio for mass-dependent isotopic fractionation,

The program applies eqn (1) and (3) to both the integrated peaks and individual data points in the integration window. With the latter, the ion intensities measured during the Rb sequence are interpolated to the times of the SrF sequence to minimize bias associated with spectral skew. The values of ${}^{87}\text{Rb}^+/{}^{86}\text{Sr}^+$ and ${}^{87}\text{Sr}^+/{}^{86}\text{Sr}^+$ calculated from the integrated peaks in the acquisition window are the values that the program reports for each sample. The values of ${}^{87}\text{Rb}^+/{}^{86}\text{Sr}^+_i$ and ${}^{87}\text{Sr}^+/{}^{86}\text{Sr}^+_i$ for each cycle (*i* denotes the SrF cycles, of which there are *n* in total in the acquisition window) are used to estimate the standard deviations of the mean,

$$\sigma_{^{87}\text{Rb}^+/^{86}\text{Sr}^+} = \sigma_{^{87}\text{Rb}^+/^{86}\text{Sr}^+_{i}} / \sqrt{n}, \tag{4}$$

$$\sigma_{^{87}\mathrm{Sr}^+}/^{^{86}\mathrm{Sr}^+} = \sigma_{^{87}\mathrm{Sr}^+}/^{^{86}\mathrm{Sr}^+}/\sqrt{n},$$
(5)

as well as the correlation coefficient

$$\rho = \frac{\operatorname{cov}\left({}^{87}\mathrm{Rb}^{+}/{}^{86}\mathrm{Sr}^{+}{}_{i}, {}^{87}\mathrm{Sr}^{+}/{}^{86}\mathrm{Sr}^{+}{}_{i}\right)}{\sqrt{\operatorname{var}\left({}^{87}\mathrm{Rb}^{+}/{}^{86}\mathrm{Sr}^{+}{}_{i}\right)\operatorname{var}\left({}^{87}\mathrm{Sr}^{+}/{}^{86}\mathrm{Sr}^{+}{}_{i}\right)}}.$$
(6)

Once the user has cycled through all the laser ablation measurements, the software exports an *xlsx* file that contains the reduced data for each sample.

Silicate glass standards SRM610 and feldspar glass H (FGH) from Davidson et al. (2001)33 were used to bracket the sample measurements. The major element composition of SRM610 is \sim 72 wt% SiO₂, 14 wt% Na₂O, 12 wt% CaO, and 2 wt% Al₂O₃, which is not representative of chemical compositions encountered in nature. It contains 425.7 ppm Rb and 515.5 ppm Sr. It was used here because its ⁸⁷Rb/⁸⁶Sr and ⁸⁷Sr/⁸⁶Sr ratios are well known (2.3894 and 0.709699, respectively⁶⁰), it was used previously in in situ 87Rb-87Sr studies, and it has near homogeneous composition. We also used a plagioclase glass standard (FGH) that had been prepared by Davidson et al. (2001)33 by melting plagioclase grains extracted from a sample from Mt Pelée (M8230 from ref. 61) and doping the sample with Rb. It contains ${\sim}262$ ppm Rb and ${\sim}506$ ppm Sr. Its $^{87}\text{Rb}/^{86}\text{Sr}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are 1.500986 and 0.704193, respectively.33 The matrix composition of this standard is a better match for the rocks and minerals that we measured here, but its level of homogeneity is unknown, especially for the ⁸⁷Rb/⁸⁶Sr ratio. We adopted SRM610 normalization as our preferred normalization scheme for reasons that are discussed below, notably because the secondary correction to the Shap granite is smaller with SRM610, but the data reduced using bracketing by FGH are also compiled in data tables and plotted in some figures for comparison, and the results agree within uncertainty.

$$\frac{{}^{87}\text{Sr}^{+}}{{}^{86}\text{Sr}^{+}} = \frac{{}^{87}\text{Sr}^{19}\text{F}^{+} - {}^{85}\text{Rb}^{19}\text{F}^{+}(0.2783/0.7217)(86.90918053/84.91178974)^{\beta_{\text{Sr}}}}{{}^{86}\text{Sr}^{19}\text{F}^{+}} \bigg/ \bigg(\frac{86.90887750}{85.90926073}\bigg)^{\beta_{\text{Sr}}}.$$
(3)

Most of the measurements were performed in sequences of 5 sample laser spot measurements bracketed by spot measurements of FGH and SRM610 in a sequence FGH–SRM610–spot1–spot2–spot3–spot4–spot5–FGH–SRM610. The 87 Rb⁺/ 86 Sr⁺ and internally normalized 87 Sr⁺/ 86 Sr⁺ ratios were further corrected by bracketing with the standards using the formulas,

$$\begin{pmatrix} \frac{8^{7}Rb}{8^{6}Sr} \\ \frac{2(8^{7}Rb^{+}/8^{6}Sr^{+})_{spot \ i}}{(8^{7}Rb^{+}/8^{6}Sr^{+})_{STD \ 1} + (8^{7}Rb^{+}/8^{6}Sr^{+})_{STD \ 2}} \begin{pmatrix} \frac{8^{7}Rb}{8^{6}Sr} \\ \frac{8^{7}Sr}{8^{6}Sr} \\ \frac{2(8^{7}Sr^{+}/8^{6}Sr^{+})_{spot \ i}}{(8^{7}Sr^{+}/8^{6}Sr^{+})_{STD \ 1} + (8^{7}Sr^{+}/8^{6}Sr^{+})_{STD \ 2}} \begin{pmatrix} \frac{8^{7}Rb}{8^{6}Sr} \\ \frac{8^{7}Rb}{8^{6}Sr} \\ \frac{8^{7}Sr}{8^{6}Sr^{+}} \\ \frac{8^{7}Sr^{+}/8^{6}Sr^{+}}{(8^{7}Sr^{+}/8^{6}Sr^{+})_{STD \ 2}} \end{pmatrix}_{STD \ 2} \begin{pmatrix} \frac{8^{7}Rb}{8^{6}Sr} \\ \frac{8^{7}Sr}{8^{6}Sr} \\ \frac{8^{7}Sr}{8^{5}Sr} \end{pmatrix}_{STD},$$
(8)

where STD 1 and STD 2 denote the two standard spot measurements (either SRM610 or FGH) that bracket the sample spot measurement, while $({}^{87}\text{Rb}/{}^{86}\text{Sr})_{\text{STD}}$ and $({}^{87}\text{Sr}/{}^{86}\text{Sr})_{\text{STD}}$ are the recommended values for either SRM610 or FGH.

Both the sample and standard spot analyses are affected by uncertainties that need to be propagated in eqn (7) and (8). For ⁸⁷Rb–⁸⁷Sr dating, it is particularly important to evaluate the extent to which the errors are correlated, as this affects calculated ages and goodness-of-fit estimates. The errors in ⁸⁷Rb/⁸⁶Sr

⁸⁷Rb/⁸⁶Sr, associated with some spread in ⁸⁷Sr/⁸⁶Sr from ⁸⁷Rb decay that should fall along the isochron. (ii) The two ratios ⁸⁷Rb/⁸⁶Sr and ⁸⁷Sr/⁸⁶Sr ratios share the same denominator isotope (⁸⁶Sr), which can induce some statistical correlation between the two ratios (see the Appendix in ref. 62).

In the following, *S* denotes 87 Sr/ 86 Sr ratios, while *R* denotes 87 Rb/ 86 Sr ratios. The sample measurements (subscript 1) are bracketed by two standard measurements (subscripts 2 and 3) with know 87 Sr/ 86 Sr and 87 Rb/ 86 Sr ratios (noted *s* and *r* respectively). The 87 Sr/ 86 Sr and 87 Rb/ 86 Sr ratios of the sample corrected by standard bracketing are given by,

$$S_1^* = \frac{2sS_1}{S_2 + S_3},\tag{9}$$

$$R_1^* = \frac{2rR_1}{R_2 + R_3}.$$
 (10)

We note \mathbf{g} the function that gives the corrected ratios from the measured ratios,

$$\mathbf{g}(S_1, S_2, S_3, R_1, R_2, R_3) = (S_1^*, R_1^*).$$
(11)

To calculate the uncertainties on the ages and intercepts of 87 Sr/ 86 Sr and 87 Rb/ 86 Sr isochrons, we need to propagate the uncertainties on S_1 , S_2 , S_3 , R_1 , R_2 , and R_3 onto S_1^* and R_1^* . This is done using the delta method. The gradient matrix of **g** is,

$$\nabla \mathbf{g} = \begin{bmatrix} \frac{2s}{S_2 + S_3} & \frac{-2sS_1}{(S_2 + S_3)^2} & \frac{-2sS_1}{(S_2 + S_3)^2} & 0 & 0 & 0\\ 0 & 0 & 0 & \frac{2r}{R_2 + R_3} & \frac{-2rR_1}{(R_2 + R_3)^2} & \frac{-2rR_1}{(R_2 + R_3)^2} \end{bmatrix}.$$
 (12)

and ⁸⁷Sr/⁸⁶Sr could be correlated for two reasons: (i) during a spot analysis of heterogeneous material, different minerals or mineral domains ablated at one spot can have variable

Because S_1 - R_1 , S_2 - R_2 , and S_3 - R_3 are the only dependent variable pairs, the covariance matrix for $(S_1, S_2, S_3, R_1, R_2, R_3)$ is,

$$\boldsymbol{\Sigma} = \begin{bmatrix} \operatorname{Cov}(S_1, S_1) & 0 & 0 & \operatorname{Cov}(S_1, R_1) & 0 & 0 \\ 0 & \operatorname{Cov}(S_2, S_2) & 0 & 0 & \operatorname{Cov}(S_2, R_2) & 0 \\ 0 & 0 & \operatorname{Cov}(S_3, S_3) & 0 & 0 & \operatorname{Cov}(S_3, R_3) \\ \operatorname{Cov}(S_1, R_1) & 0 & 0 & \operatorname{Cov}(R_1, R_1) & 0 & 0 \\ 0 & \operatorname{Cov}(S_2, R_2) & 0 & 0 & \operatorname{Cov}(R_2, R_2) & 0 \\ 0 & 0 & \operatorname{Cov}(S_3, R_3) & 0 & 0 & \operatorname{Cov}(R_3, R_3) \end{bmatrix}.$$
(13)

The delta method gives an approximation of the covariance matrix **V** for (S_1^*, R_1^*) ,

$$\mathbf{V} = \begin{bmatrix} \operatorname{Cov}(S_1^*, S_1^*) & \operatorname{Cov}(S_1^*, R_1^*) \\ \operatorname{Cov}(S_1^*, R_1^*) & \operatorname{Cov}(R_1^*, R_1^*) \end{bmatrix} \simeq \nabla \mathbf{g} \cdot \mathbf{\Sigma} \cdot \nabla \mathbf{g}^{\mathrm{T}}, \quad (14)$$

and we have,

Paper

$$\operatorname{Var}(S_{1}^{*}) \simeq S_{1}^{*2} \left\{ \frac{\operatorname{Var}(S_{1})}{S_{1}^{2}} + \frac{\operatorname{Var}(S_{2}) + \operatorname{Var}(S_{3})}{(S_{2} + S_{3})^{2}} \right\}, \quad (15)$$

spot measurements by calculating the slope of two-point isochrons connecting a particular spot analysis and the isochron intercept defined by all the points,

$$t^* = \frac{1}{\lambda_{^{87}\text{Rb}}} \ln \left(1 + \frac{{}^{87}\text{Sr}/{}^{86}\text{Sr} - {}^{87}\text{Sr}/{}^{86}\text{Sr}_0}{{}^{87}\text{Rb}/{}^{86}\text{Sr}} \right).$$
(22)

where $\lambda_{^{87}Rb}$ is the decay constant of ^{87}Rb of 0.000013972 per million year.^{1,2} To calculate the uncertainty on this model age, it is again important to consider the correlation between the $^{87}Rb/^{86}Sr$ and $^{87}Sr/^{86}Sr$ errors and we have,

$$\sigma_{t^*}/t^* \simeq \sqrt{\left(\frac{\sigma_{^{87}\text{Rb}}/^{^{86}\text{Sr}}}{^{87}\text{Rb}/^{^{86}\text{Sr}}}\right)^2 + \left(\frac{\sigma_{^{87}\text{Sr}}/^{^{86}\text{Sr}}}{^{87}\text{Sr}/^{86}\text{Sr}_0}\right)^2 - 2\rho \left(\frac{\sigma_{^{87}\text{Rb}}/^{^{86}\text{Sr}}}{^{87}\text{Rb}/^{^{86}\text{Sr}}}\right) \left(\frac{\sigma_{^{87}\text{Sr}}/^{^{86}\text{Sr}}}{^{87}\text{Sr}/^{^{86}\text{Sr}}}\right).$$
(23)

$$\operatorname{Var}(R_{1}^{*}) \simeq R_{1}^{*2} \left\{ \frac{\operatorname{Var}(R_{1})}{R_{1}^{2}} + \frac{\operatorname{Var}(R_{2}) + \operatorname{Var}(R_{3})}{(R_{2} + R_{3})^{2}} \right\}, \quad (16)$$

$$\operatorname{Cov}(S_1^*, R_1^*) \simeq S_1^* R_1^* \bigg\{ \frac{\operatorname{Cov}(S_1, R_1)}{S_1 R_1} + \frac{\operatorname{Cov}(S_2, R_2) + \operatorname{Cov}(S_3, R_3)}{(R_2 + R_3)(S_2 + S_3)} \bigg\}.$$
(17)

The *IsoplotR* program uses standard deviations $\sigma_X = \sqrt{\operatorname{Var}(X)}$ and correlation coefficients $\rho_{X,Y} = \operatorname{Cov}(X,Y)/(\sigma_X \sigma_Y)$ as inputs in isochron calculations. The equations above can be reformulated with those notations and we have,

$$\sigma_{S_1^*} \simeq S_1^* \sqrt{\frac{\sigma_{S_1}^2}{S_1^2} + \frac{\sigma_{S_2}^2 + \sigma_{S_3}^2}{(S_2 + S_3)^2}},$$
(18)

$$\sigma_{R_1^*} \simeq R_1^* \sqrt{\frac{\sigma_{R_1}^2}{R_1^2} + \frac{\sigma_{R_2}^2 + \sigma_{R_3}^2}{(R_2 + R_3)^2}},$$
(19)

$$\rho_{S^*,P^*} \simeq \frac{\frac{\rho_{S_1,R_1}\sigma_{S_1}\sigma_{R_1}}{S_1R_1} + \frac{\rho_{S_2,R_2}\sigma_{S_2}\sigma_{R_2} + \rho_{S_3,R_3}\sigma_{S_3}\sigma_{R_3}}{(R_2 + R_3)(S_2 + S_3)}}{(R_2 + R_3)(S_2 + S_3)}, \quad (20)$$

$$\sqrt{\left\{\frac{\sigma_{S_1^2}}{S_1^2} + \frac{\sigma_{S_2^2} + \sigma_{S_3^2}}{(S_2 + S_3)^2}\right\} \left\{\frac{\sigma_{R_1^2}}{R_1^2} + \frac{\sigma_{R_2^2} + \sigma_{R_3^2}}{(R_2 + R_3)^2}\right\}}.$$

3. Results

3.1. Analysis of reference materials with known compositions

We applied the method outlined above to several reference materials with known 87Rb/86Sr and 87Sr/86Sr ratios: Durango apatite,64 SRM612,60 feldspar glasses I and L2.33 Durango apatite contains \sim 475 Sr with an 87 Sr/ 86 Sr ratio of 0.70633 and 87 Rb/ 86 Sr \sim 0.64 FGI was made from the same Mt Pelée plagioclase as FGH described above, but it contains different amounts of Rb (~142 ppm) and Sr (~501 ppm). Its ⁸⁷Rb/⁸⁶Sr and ⁸⁷Sr/⁸⁶Sr ratios are 0.82234 and 0.704137 \pm 12, respectively.³³ FGL2 was made from plagioclase separated from a volcanic rock from El Chichón (DT-5), which was doped with Rb. The Rb and Sr concentrations in that glass are \sim 75 and \sim 2058 ppm with 87 Rb/ 86 Sr and 87 Sr/ 86 Sr ratios of 0.10550 and 0.704335 \pm 17, respectively.³³ The degree of homogeneity in FGI and FGL2 are unknown. SRM612 has the same major element composition as SRM610 (~72 wt% SiO2, 14% Na₂O, 12% CaO, and 2% Al₂O₃) but lower trace element content (31.4 ppm Rb and 78.4 ppm Sr). Its ⁸⁷Rb/⁸⁶Sr and ⁸⁷Sr/⁸⁶Sr ratios are 1.15766 and 0.709063, respectively.60 We plot in Fig. 4 the measured ⁸⁷Rb/⁸⁶Sr and ⁸⁷Sr/⁸⁶Sr ratios against previously published values using both SRM610 and FGH bracketing normalizations. Depending on the standard used, we find small departures in ⁸⁷Sr/⁸⁶Sr ratios from recommended values (Fig. 4B)

$$\rho_{S_{1}^{*},R_{1}^{*}} \simeq \frac{(S_{2}+S_{3})(R_{2}+R_{3}) \rho_{S_{1},R_{1}}\sigma_{S_{1}}\sigma_{R_{1}} + S_{1}R_{1} \left(\rho_{S_{2},R_{2}}\sigma_{S_{2}}\sigma_{R_{2}} + \rho_{S_{3},R_{3}}\sigma_{S_{3}}\sigma_{R_{3}}\right)}{\sqrt{\left\{(S_{2}+S_{3})^{2}\sigma_{S_{1}}^{2} + S_{1}^{2}\sigma_{S_{2}}^{2} + S_{1}^{2}\sigma_{S_{3}}^{2}\right\}\left\{(R_{2}+R_{3})^{2}\sigma_{R_{1}}^{2} + R_{1}^{2}\sigma_{R_{2}}^{2} + R_{1}^{2}\sigma_{R_{3}}^{2}\right\}}}.$$
(21)

The *IsoplotR* program was used to calculate the intercepts (initial ⁸⁷Sr/⁸⁶Sr ratios) and slopes (ages) of the ⁸⁷Rb-⁸⁷Sr isochrons.⁶³ We have also calculated model ages for individual

but the 87 Sr/ 86 Sr data remain accurate within $\sim \pm 0.001$. This level of accuracy is sufficient for most applications as natural variations in 87 Sr/ 86 Sr span a large range. The reason for the small observed departures is difficult to establish but could be due to (i)

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Fig. 4 Comparison between previously published and measured ⁸⁷Rb/⁸⁶Sr (A) and ⁸⁷Sr/⁸⁶Sr (B) ratios in Durango apatite (DA), feldspar glass I and L2 (FGI, FGL2), and SRM612. The black filled circles use SRM610 for correction of instrumental fractionation. The red filled circles use feldspar glass H (FGH) for correction. The solid lines are 1 : 1 correlations. The reference values for SRM612, Durango apatite, Feldspar glasses I and L2 are from Woodhead and Hergt,⁶⁰ Yang *et al.*,⁶⁴ and Davidson *et al.*³³

inadequate correction of mass-dependent fractionation using the exponential law, or (ii) a small isobaric interference on Sr isotopes. The first explanation is unlikely because the predicted effect would be smaller than what is measured given the range of mass-dependent fractionation affecting Sr isotopes in MC-ICP-MS/MS.⁶⁵ We find no correlation between Rb/Sr and departure of 87 Sr/ 86 Sr from recommended values, suggesting that the presence of an interference from 87 RbF⁺ on 87 SrF⁺ is unlikely. We cannot exclude, however, the presence of a yet unidentified interference on Sr isotopes. Evaluating the accuracy of 87 Rb/ 86 Sr ratio measurements is more difficult as the homogeneity of FGI and FGL2 has not been tested but we find reasonable agreement between published and measured values.

3.2. Comparison between measurement uncertainties and theoretical limit from counting statistics and Johnson noise

In Sr isotopic analysis by MC-ICP-MS, instability in instrumental mass bias is the main source of variation in raw isotopic ratios, but it is corrected for by internal normalization using the 88Sr/86Sr ratio. The remaining uncertainty in internally normalized ⁸⁷Sr/⁸⁶Sr ratios can be due to counting statistics, Johnson noise associated with thermal agitation of free electrons, variations in the law describing mass fractionation in the mass spectrometer, and unresolved isobaric interferences. Errors arising from counting statistics and Johnson noise are unavoidable and represent the foundation of what precision is theoretically achievable. Below, we compare the measured precision of isotopic analyses with the theoretical limit from counting statistics and Johnson noise by adapting the formulas derived by Dauphas et al.62 to a transient signal with blank subtraction. The blank is measured at the beginning of the laser ablation over $N_{\rm b}$ cycles (index p) of duration Δt each. The sample is measured as a transient signal after the blank over N_s cycles (index *j*) of duration Δt each. The total number of counts n_i for isotope *i* is obtained by subtracting from the sample counts the blank counts scaled to the same analysis duration as the sample,

$$n_{i} = \sum_{j} n_{i,j} - \frac{t_{s}}{t_{b}} \sum_{p} n_{i,p} = \sum_{j} \frac{U_{i,j}}{eR_{i}} \Delta t - \frac{N_{s}}{N_{b}} \sum_{p} \frac{U_{i,p}}{eR_{i}} \Delta t$$
$$= \frac{\overline{U}_{i,s}t_{s}}{eR_{i}} - \frac{\overline{U}_{i,b}t_{s}}{eR_{i}}, \qquad (24)$$

where $U_{i,q}$ is the voltage (in V) measured for isotope *i* during cycle *q* (*j* and *p* correspond to sample and blank cycle measurements), R_i is the value of the resistor (in Ω) used to measure isotope *i*, *e* is the elementary charge (1.602 × 10⁻¹⁹ C), $t_s = N_s \Delta t$, $t_b = N_b \Delta t$, $\overline{U}_{i,s} = \sum_j U_{i,j}/N_s$, and $\overline{U}_{i,b} = \sum_p U_{i,p}/N_b$. The uncertainties associated with counting statistics and Johnson noise during a cycle (blank or sample) are,

$$\sigma_{\text{counting},i,q}^{2} = n_{i,q} = U_{i,q} \Delta t / e R_{i}, \qquad (25)$$

$$\sigma_{\text{Johnson},i,q}^{2} = 4kT\Delta t/e^{2}R_{i},$$
(26)

where k is Boltzmann constant (1.380649 \times 10⁻²³ m² kg s⁻² K⁻¹) and T is the temperature of the resistor in K. There uncertainties add up quadratically over all cycles and we have,

$$\sigma_{n_i}^2 = \frac{\overline{U}_{i,s}t_s}{eR_i} + \frac{4kTt_s}{e^2R_i} + \frac{\overline{U}_{i,b}t_s^2}{eR_it_b} + \frac{4kTt_s^2}{e^2R_it_b}.$$
 (27)

We use the following notations,

$$X_{i} = \frac{\sigma_{i}^{2}}{n_{i}^{2}}$$

$$= \frac{\overline{U}_{i,s}eR_{i}}{\left(\overline{U}_{i,s} - \overline{U}_{i,b}\right)^{2}t_{s}} + \frac{4kTR_{i}}{\left(\overline{U}_{i,s} - \overline{U}_{i,b}\right)^{2}t_{s}} + \frac{\overline{U}_{i,b}eR_{i}}{\left(\overline{U}_{i,s} - \overline{U}_{i,b}\right)^{2}t_{b}}$$

$$+ \frac{4kTR_{i}}{\left(\overline{U}_{i,s} - \overline{U}_{i,b}\right)^{2}t_{b}} \approx \frac{eR_{i}}{\overline{U}_{i,s}t_{s}} + \frac{4kTR_{i}}{\overline{U}_{i,s}^{2}t_{s}} + \frac{\overline{U}_{i,b}eR_{i}}{\overline{U}_{i,s}^{2}t_{b}} + \frac{4kTR_{i}}{\overline{U}_{i,s}^{2}t_{b}},$$

$$(28)$$

$$\mu_{j|i} = \ln(m_j/m_i). \tag{29}$$

The relative uncertainties on internally normalized ratios (the star superscript in ⁸⁴Sr/⁸⁶Sr* and ⁸⁷Sr/⁸⁶Sr* indicates that those ratios are internally normalized) from counting statistics and Johnson noise are,⁶²

$$\frac{\sigma_{^{87}\mathrm{Sr}/^{86}\mathrm{Sr}^*}}{^{87}\mathrm{Sr}/^{86}\mathrm{Sr}^*} = \sqrt{X_{^{87}\mathrm{Sr}} + \left(\frac{\mu_{^{87/86}}}{\mu_{^{88/86}}}\right)^2 X_{^{88}\mathrm{Sr}} + \left(\frac{\mu_{^{87/86}}}{\mu_{^{88/86}}}\right)^2 X_{^{86}\mathrm{Sr}}, \quad (30)$$

$$\frac{\sigma_{^{87}\mathrm{Sr}/^{86}\mathrm{Sr}^*}}{^{87}\mathrm{Sr}/^{86}\mathrm{Sr}^*} \simeq \sqrt{X_{^{87}\mathrm{Sr}} + 0.25X_{^{88}\mathrm{Sr}} + 0.25X_{^{86}\mathrm{Sr}}},$$
(31)

$$\frac{\sigma_{^{84}\mathrm{Sr}/^{86}\mathrm{Sr}^*}}{^{84}\mathrm{Sr}/^{86}\mathrm{Sr}^*} = \sqrt{X_{^{84}\mathrm{Sr}} + \left(\frac{\mu_{^{84/86}}}{\mu_{^{88/86}}}\right)^2 X_{^{88}\mathrm{Sr}} + \left(\frac{\mu_{^{84/88}}}{\mu_{^{88/86}}}\right)^2 X_{^{86}\mathrm{Sr}}},\quad(32)$$

$$\frac{\sigma_{^{84}\mathrm{Sr}}/^{86}\mathrm{Sr}^*}{^{84}\mathrm{Sr}/^{86}\mathrm{Sr}^*} \simeq \sqrt{X_{^{84}\mathrm{Sr}} + X_{^{88}\mathrm{Sr}} + 4X_{^{86}\mathrm{Sr}}},$$
(33)

We have calculated the precision achieved during Sr-only isotopic analysis of standards SRM610, SRM612, and Durango apatite. This was done in two manners: (i) all standards were analyzed on 5 to 10 spots each, and we calculated the standard deviation of those analyses (spot-level uncertainty). (ii) Each spot analysis is divided into cycles, and we calculated the standard deviation of the mean of all cycles for each spot analysis (cycle-level uncertainty). We also applied eqn (28) and (31) to calculate the theoretical limit on precision for conditions relevant to our Sr isotopic analyses (blank measured over 28 cycles of 1 s each with 0.0025 V on 86, 0.00030 V on 87, and 0.003 V on 88; sample measured over 56 cycles of 1 s each, all isotopes measured on $10^{11} \Omega$ resistors; the temperature of the resistors set to 42 °C). We calculated the theoretical error with (eqn (28)) or without (the last two terms dropped from eqn (28)) the blank error included. This calculation shows that for those conditions, Johnson noise should become the dominant source of uncertainty when ⁸⁸Sr is at less than \sim 1.2 V, which corresponds to 0.14 V on ⁸⁶Sr and 0.10 V on ⁸⁷Sr. We compare in Fig. 5 the theoretical limit with the precisions achieved. As shown, there is excellent agreement between the blank-free theoretical limit and the precision calculated from the standard deviation of the mean of the cycle-level analyses. The precision calculated from the standard deviation of the spot-level analyses is also close but is slightly higher. Adding the uncertainty arising from the blank brings the theoretical expectation in closer agreement with the spot-level uncertainty. This makes sense as the main difference between the cycle-level and spot-level uncertainties is blank subtraction. The same blank is subtracted from all cycles measured at one spot, so blank subtraction is not a source of scatter at the cycle level. In spot analyses a different blank is subtracted for each analysis, so it contributes to the scatter. Overall, our standard measurements have precisions that are close to the theoretical limit.



Fig. 5 Comparison between actual measurement precision on internally normalized ⁸⁷Sr/⁸⁶Sr for SRM610, SRM612, and Durango apatite, with theoretical limit from Johnson noise and counting statistics (egn (31)⁶²). The dashed grey lines are the theoretical limits for Johnson noise (dominant below ~1.2 V on ⁸⁸Sr) and counting statistics (dominant above \sim 1.2 V) when the blank uncertainty is not included (excluding the last two terms in eqn (28)). The red line combines those errors quadratically. The dashed red line shows the effects of Johnson noise and counting statistics when the blank uncertainty is included (egn (28); the added uncertainty arises primarily from Johnson noise on the blank). The light red filled squares were calculated from the standard deviation of the mean of cycle analyses. The dark red filled circles were calculated from 5 to 10 repeat analyses of the same standard. The main difference between cycle- and spot-level dispersion is removal of a different blank for each spot analysis. The precision on ⁸⁷Sr/⁸⁶Sr achievable by LA-MC-ICP-MS/MS is close to the theoretical limit.

3.3. Secondary calibration to the Shap granite isochron

A significant difficulty in in situ ⁸⁷Rb-⁸⁷Sr analysis by LA-MC-ICP-MS/MS is the fractionation of Rb/Sr induced by the laser ablation and plasma torch. While we apply a first-order correction for this fractionation by bracketing the sample laser ablation analyses by standard analyses (SRM610 and FGH) of known compositions, inaccuracy can persist due to mismatch in matrix composition/structure and possible heterogeneity for FGH. Bevan et al.51 used the approach of measuring isochrons in materials of known ages and similar mineralogy/composition to apply a correction factor on the ⁸⁷Rb/⁸⁶Sr ratio. As discussed below, we have applied in situ ⁸⁷Rb-⁸⁷Sr dating to Martian meteorite NWA 7034, where the isochron slope is determined by K-rich feldspars, which match neither SRM610 nor FGH chemically. The K-rich feldspar in NWA 7034 has a composition Or₇₇Ab₂₁An₃ (Meteoritical Bulletin), well within the field of K-feldspar polymorphs orthoclase, sanidine, and microcline. To appropriately correct



Fig. 6 87 Rb/ 86 Sr (right axis; orange symbols) and 87 Sr/ 86 Sr (left axis; blue symbols) ratios (A) along a transect in a K-feldspar megacryst from the Shap granite (B). The small, filled circles and lines are LA-MC-ICP-MS/MS data, while the large symbols are measurements from Davidson *et al.*⁶⁷ acquired by TIMS on micromilled samples along the same transects (black holes in panel (B) for the inner core, outer core, inner rim, and outer rim). Panel (B) shows a false color image generated by data acquired on an SEM. Yellow is orthoclase, green is albite, blue is guartz, and red is biotite. The 87 Sr/ 86 Sr variations stem primarily from 87 Rb-decay after crystallization (Fig. 7, ref. 67). The 100 µm laser ablation spots inside (transects) and outside the megacryst are shown as white-filled circles.

for matrix effects on ⁸⁷Rb-⁸⁷Sr, we have measured the Shap granite, with emphasis on orthoclase which has a bulk composition Or75.0Ab24.6An0.4 (ref. 66) that is very close to the composition of alkali-feldspars in NWA 7034. A second reason why we decided to study Shap granite is that it was previously dated by *in situ*⁸⁷Rb-⁸⁷Sr using the Proteus instrument⁵¹ and by micromilling followed by TIMS.67 The Shap granite has an ⁸⁷Rb/⁸⁶Sr isochron age of ~397 Ma.⁶⁸ The measurements presented here were acquired on the very same specimen analyzed by Davidson *et al.*,⁶⁷ who obtained an age of 405 ± 2 Ma and an initial 87 Sr/ 86 Sr ratio of ~0.7072. The mount analyzed by Davidson et al.67 contains a large megacryst with an orthoclase core and a plagioclase (albite) rim, and a groundmass of biotite, plagioclase, and quartz. Davidson et al.67 milled four locations in the megacryst: inner orthoclase core, outer orthoclase core, inner plagioclase rim, outer plagioclase rim. We ran a transect along those previously milled spots (Fig. 6). The ⁸⁷Rb/⁸⁶Sr and

87Sr/86Sr ratios measured by LA-MC-ICP-MS/MS along this transect are plotted in Fig. 6A together with the previous TIMS measurements. As shown, there is excellent agreement between the TIMS and LA-MC-ICP-MS/MS. The ⁸⁷Rb/⁸⁶Sr and ⁸⁷Sr/⁸⁶Sr ratios follow parallel trends, which is the result of *in situ* decay of ⁸⁷Rb into ⁸⁷Sr in the megacryst. We also measured several minerals in the groundmass (see Fig. 6B for the locations of the laser spots), including several high Rb/Sr biotite crystals. The data points for the Shap granite are plotted in ⁸⁷Rb-⁸⁷Sr isochron diagrams in Fig. 7. The two normalizations to FGH and SRM610 are used in those plots. We plot the isochrons using only the megacryst data and using all data including the high Rb/Sr biotite data. Using FGH normalization, the ages obtained are 277 \pm 19 Ma (megacryst only) and 338 \pm 7 Ma (all data including biotite). This is much lower than the known age of the sample of 397 Ma, indicating either that FGH is a poor matrix match for orthoclase or that FGH is heterogeneous and the shard that we mounted has different ⁸⁷Rb/⁸⁶Sr ratio than the value measured by Davidson et al.67 Using SRM610 normalization, we obtain ages of 326 \pm 10 Ma (megacryst only) and 369 \pm 12 Ma (all data including biotite). Although the difference is smaller than when FGH is used for normalization, this is still lower than the independently know age of 397 Ma. As discussed below, for dating Martian meteorite Black Beauty, we are primarily interested in the bias associated with analyzing ⁸⁷Rb/⁸⁶Sr in K-rich feldspar, so the isochron constructed using the megacryst alone is the one most relevant. To obtain the correct age for the Shap granite megacryst, one must divide the FGH normalized 87Rb/86Sr ratio by 1.43 and the SRM610 normalized 87Rb/86Sr ratio by 1.21. Because the bias associated with SRM610 is smaller than with FGH, we adopt this normalization and use the correction factor of 1.21 to correct ⁸⁷Rb/⁸⁶Sr ratios on K-feldspar calculated based on SRM610 bracketing,

$$\frac{{}^{87}\text{Rb}^*}{{}^{86}\text{Sr}} = \frac{1}{1.21} \frac{{}^{87}\text{Rb}}{{}^{86}\text{Sr}}.$$
(34)

Bevan et al.51 calculated correction factors based on analysis of the Dartmoor granite DG-1 isochron and obtained values that ranged between 0.975 and 1.007. Although our correction is significant, the Shap granite megacryst is an excellent matrix match for K-feldspar in NWA 7034 and the correction is likely to be accurate. Bevan *et al.*⁵¹ obtained a precision of ± 2.5 Ma on their isochron of the Shap granite, which reflects in part the fact that they measured many more feldspar spots (n = 135) than we did on the Shap megacryst (n = 40) and their ⁸⁷Rb/⁸⁶Sr feldspar measurements span a much wider range (0-50) than those measured by us in the megacryst (0-4). Our best estimate for the initial ⁸⁷Sr/⁸⁶Sr ratio of 0.70821(27) is slightly higher than the values of ~0.7072 and 0.70755(4) reported by Davidson et al.67 and Bevan et al.51 As discussed in Sect. 2.4, our SRM610normalized 87Sr/86Sr ratios are expected to be accurate to within $\sim\pm0.001$, so there is no obvious discrepancy with previous studies.

Paper





Fig. 7 ⁸⁷Rb–⁸⁷Sr *in situ* isochron diagrams for the Shap granite, which is independently dated at ~397 Ma.⁶⁸ Isochron slopes and intercepts were calculated using the *IsoplotR* program. The measurements presented here were acquired on the same specimen analyzed by Davidson *et al.*⁶⁷ using micromilling and TIMS analyses. Davidson *et al.*⁶⁷ obtained an age of 405 Ma and an initial ⁸⁷Sr/⁸⁶Sr ratio of ~0.7072. In panels (A) and (C), the ⁸⁷Sr/⁸⁶Sr and ⁸⁷Rb/⁸⁶Sr ratios were corrected for instrumental fractionation by normalization to feldspar glass H (FGH) from Davidson *et al.*,³³ while panels (B) and (D) were corrected by normalization to SRM610. Panels (A) and (B) use all data, including spots analyzed on biotite with extreme ⁸⁷Rb/⁸⁶Sr ratios. Panels (A) and (D) only use data from a single orthoclase megacryst. All ages reported here are too young relative to expectations.^{67,68} The reason for the too young ages is the inadequacy of the FGH and SRM610 standards to correct for fractionation of the Rb/Sr ratio induced by laser ablation and plasma-ionization.⁵¹ To obtain the correct age for the Shap granite megacryst (orthoclase), one must divide the FGH- and SRM610-normalized ⁸⁷Rb/⁸⁶Sr ratios by 1.43 and 1.21, respectively.

The Shap granite biotite that we measured has extremely high ${}^{87}\text{Rb}/{}^{86}\text{Sr}$ ratio, which provides us with an opportunity to assess the extent to which Rb can form fluorides and the size of the effect that this induces on ${}^{87}\text{Sr}^{19}\text{F}^+$. One of the biotite that we analyzed has SRM610-normalized ${}^{87}\text{Rb}/{}^{86}\text{Sr}$ and ${}^{87}\text{Sr}/{}^{86}\text{Sr}$ ratios of 817 ± 114 and 4.871 ± 0.238 , with a correlation coefficient of ~0.6 between the two. If we artificially set ${}^{85}\text{Rb}^{19}\text{F}^+$ to 0, the ${}^{87}\text{Sr}/{}^{86}\text{Sr}$ ratio shifts to 4.879, which is well within error. Even during laser ablation of this extremely Rb-rich mineral, the ${}^{85}\text{Rb}^{19}\text{F}^+$ does not rise above the blank, corresponding to a conservative upper limit ${}^{85}\text{Rb}^{19}\text{F}^+/{}^{85}\text{Rb}^+ < 10^{-5}$. To summarize, Rb does not form fluorides and the ${}^{87}\text{Rb}\text{F}^+$ correction is always negligible.

4. Discussion

The ⁸⁷Rb-⁸⁷Sr decay system produces isotopic variations in rocks and minerals that can be used to (1) date rocks, (2) tease out the history of crustal growth on Earth, (3) trace assimilation of country rock and mixing in magmas, (4) correlate strata through isotope chemostratigraphy, (5) trace animal and human migration, and (6) trace the past exchanges of goods and artifacts. TIMS analyses of Sr isotopic compositions after Sr purification and Rb/Sr determinations by isotope dilution are the gold standards for such measurements due to their unrivalled accuracies and precisions (Sect. 3). TIMS analyses however suffer from two main limitations: ⁸⁷Rb-⁸⁷Sr dating

typically involves destructive rock disaggregation (crushing, mineral separation, and powdering), and throughput is limited by rock preparation, clean laboratory work, and isotopic data acquisition. The novel technique of LA-MC-ICP-MS/MS is minimally destructive, preserves petrographic context for the minerals analyzed, and is rapid. It opens many exciting avenues of research to study precious and small extraterrestrial samples and cultural artifacts, or to characterize many samples rapidly. Below, we show three examples of Sr isotopic analyses in natural samples where LA-MC-ICP-MS/MS data complement or even supersede TIMS data.

4.1. The age of NWA 7034 (Black Beauty)

The Martian meteorite NWA 7034 (and associated paired meteorites) is a unique polymict impact breccia.^{69–73} Its alkali element content is much higher than that of SNC meteorites and it contains differentiated igneous lithologies, including trachyandesite and basaltic andesite clasts. It is composed of a finegrained matrix that hosts several types of clasts (melt clasts probably formed by impact, igneous clasts, and protobreccia, which is thought to be recycled from more ancient breccia). A fascinating aspect of Black Beauty is the chronology of its components and what it tells us about Mars' history. U–Pb dating of zircon and baddeleyite revealed concordia ages of ~4.4 Ga and partial resetting at 1.4 Ga (also seen with U–Pb in phosphate).^{69,72,74-77} U–Pu–Xe,⁷⁸ ¹⁴⁶Sm–¹⁴²Nd and ¹⁴⁷Sm–¹⁴³Nd⁷⁹ also

point to very early formation of some components within Black Beauty. Chronometers more prone to thermal disturbance indicate much more recent resetting, with most ⁴⁰Ar-³⁹Ar ages clustering around 1.4 Ga.78,80,81 U + Th + Sm/He systematics point to even more recent resetting within the last ${\sim}150$ Ma.^{78,80-82} The 1.4 Ga age has been interpreted as the age of lithification (formation of the breccia)81 or resetting by protracted heating associated with plume magmatism.⁷⁸ The ⁸⁷Rb-⁸⁷Sr system complicates chronological inferences even further as the isochron obtained by Agee et al.⁷⁰ on mineral separates yielded an age of 2.089 \pm 0.081 Ga. The mineral separates analyzed by Agee et al.⁷⁰ are mixtures of minerals comprising dark (Fe,Mg-rich) and light (apatite, feldspar) colored minerals. Nyquist *et al.*⁷⁹ also studied ⁸⁷Rb–⁸⁷Sr in Black Beauty fragments and found evidence of disturbance in plagioclase. The samples measured by Nyquist et al.⁷⁹ spanned a narrower range of 87 Rb/ 86 Sr ratio (up to \sim 0.6) than the samples measured by Agee et al.⁷⁰ (up to \sim 1.8) but the reason for the discrepancy between the two studies is unclear as Agee et al.70 found no evidence for disturbance in their 4-point isochron.

The diversity of ages recorded by the various components and chronometers in Black Beauty shows that this meteorite had a complex history punctuated by major thermal disturbances. A major question that is largely unaddressed is the significance of the 2.1 Ga⁸⁷Rb-⁸⁷Sr age measured by Agee *et al.*⁷⁰ Is this age reliable? Does it reflect the time of lithification of the



Fig. 8 Petrography the NWA 7034 (Black Beauty) sample used in this study. Right: False-color Mg–Ca–Al image of Black Beauty. The Al-rich, Mg-poor grains are alkali feldspars. This map was calculated from EDS QuantMap quantitative maps acquired on a TESCAN LYRA3 field emission scanning electron microscope. Left: Reflected light image. Different clast types described in previous studies^{71–73} are indicated with labels (sp = dark melt spherules, m = dark melt clasts, cm = crystallized melt clasts, f = angular mineral fragments). Olivine-rich clasts (oc) are also present in the sample that to our knowledge have not been described before. As a guide for the analysis of alkali-rich phases we used the K concentration map to mark grains of at least 30 μ m equivalent diameter that contain 5 wt% K or more (in red on the left panel).

breccia, in which case 1.4 Ga ⁴⁰Ar-³⁹Ar ages could reflect later impact resetting?

Black Beauty is ideally suited for in situ ⁸⁷Rb-⁸⁷Sr dating by LA-MC-ICP-MS/MS as it contains K-rich feldspars that are old enough to have accumulated significant radiogenic ⁸⁷Sr and the question addressed can be easily resolved with the precision attainable with this technique. K-rich feldspars are found both within larger igneous clasts and as individual grains dispersed in the matrix. An advantage of *in situ* ⁸⁷Rb-⁸⁷Sr dating is that one can measure ages on individual crystals of various sizes and compositions to evaluate whether some have experienced resetting, which could help refine our understanding of the thermal history of Black Beauty. The sample analyzed here (FMNH ME 6118.2) is \sim 2.5 cm across and composed of diverse clasts of igneous and impact-ejecta origins (Fig. 8). Its most striking feature is the presence of a large olivine-rich clast (oc in Fig. 8; named Valentine due to its resemblance to a heart in false color image), which to our knowledge has not been documented before in other sections of NWA 7034 and paired meteorites. Our focus here are K-rich feldspars, as K and Rb have nearly identical behaviors in igneous systems.83 To identify these grains, we acquired highresolution (\sim 4.656 µm per pixel) quantitative chemical maps (Oxford Instruments AZTec QuantMap) of our section using a TESCAN LYRA3 field emission scanning electron microscope equipped with two Oxford Instrument XMax 80 silicon drift energy dispersive X-ray spectroscopy (EDS) detectors. A lower resolution QuantMap was generated by binning the pixels in batches of 4×4 corresponding to a resolution of \sim 18.624 µm per pixel. The chemical maps were then imported in Mathematica for further processing. The maps were convoluted with a circular flat kernel of 100 µm diameter to simulate analysis with a 100 µm laser ablation spot size. The convoluted K₂O and CaO chemical maps are shown in Fig. 9. We used these maps to estimate ⁸⁷Rb/⁸⁶Sr ratios in potential laser ablation spots as Rb and K have very similar geochemical behaviors, and Sr and Ca also have somewhat similar behaviors. To calculate the "87Rb/86Sr" ratio map in Fig. 9, we take the K₂O/CaO ratio and multiply it by an empirical factor relating the ⁸⁷Rb/⁸⁶Sr ratio measured by laser ablation and the K₂O/CaO ratio measured by EDS either before (by relocation of the LA spots) or after (by analysis of the LA pit) laser ablation (Fig. 10). A *Mathematica* script was used to detect grains that were at least 5 wt% K and have an equivalent diameter of at least 30 µm. By grain, we mean contiguous pixels that fulfill the criterion of K >5 wt%. The map of K-rich grains was superposed on an optical image of the Black Beauty section (Fig. 8). The K₂O/CaO ratio



Fig. 10 Relationship between the 87 Rb/ 86 Sr ratio measured by laser ablation in Black Beauty and the K₂O/CaO ratio measured in (1) the laser ablation pit by EDS analysis on a SEM or (2) through EDS mapping before laser ablation by locating the places where the measurements were made on a chemical map acquired before LA analysis. The Martian K/Rb ratio of 298 g g⁻¹ (ref. 83) and Ca/Sr ratio of 1170 g g⁻¹ (ref. 111) would yield a slope of 13, which is steeper than the slope measured here. K and Rb behave very similarly, but Ca and Sr can have different geochemical behaviors.



Fig. 9 False color maps of K₂O, CaO, and "⁸⁷Rb/⁸⁶Sr" for Black Beauty generated from QuantMap data. The third map was calculated based on an observed correlation between K₂O/CaO measured by EDS and ⁸⁷Rb/⁸⁶Sr ratio measured by ICP-MS at the laser spots (⁸⁷Rb/⁸⁶Sr \approx 1.4 K₂Owt%/ CaOwt%; Fig. 10). The black spots in the third panel (log₁₀["⁸⁷Rb/⁸⁶Sr"]) correspond approximately to the positions of the laser beam spots. The resolution of the original EDS map was downgraded by convoluting the original data by a flat circular kernel of 100 µm diameter to simulate signal averaging under the laser beam.

("⁸⁷Rb/⁸⁶Sr") and K-rich grain maps were used to identify the grains that were targeted for Sr isotopic analyses. We also measured K-poor and Ca-rich minerals to precisely define the isochron intercept.

In Fig. 11, we plot the data in an ⁸⁷Rb/⁸⁷Sr-⁸⁷Sr/⁸⁶Sr isochron diagram. Calculation of the isochron parameters was done using IsoplotR. As shown, the K-rich feldspars have ⁸⁷Rb/⁸⁶Sr ratios that extend to much higher values (\sim 37) than what had been measured previously by Agee et al.⁷⁰ (~1.8) and Nyquist et al.⁷⁹ (~0.6). We find a clear correlation between ⁸⁷Rb/⁸⁷Sr-⁸⁷Sr/⁸⁶Sr, defining an age of 2.190 \pm 0.059 Ga. This age is identical within error to the age of 2.089 \pm 0.081 Ga obtained by Agee *et al.*⁷⁰ on a 4-point mineral separate isochron. We obtain an intercept of 0.71188 \pm 0.0169, which agrees within error with the intercept of 0.71359 ± 0.00054 obtained by Agee *et al.*⁷⁰ for dark–light mineral separates. The isochron age and intercept were calculated using the method "maximum likelihood regression with overdispersion" of IsoplotR. The reason for the overdispersion (~0.008 in ⁸⁷Sr/⁸⁶Sr) is unclear and could result from geological scatter or underestimation of the analytical uncertainty. As discussed in Section 2.4, we estimate the accuracy of our ⁸⁷Sr/⁸⁶Sr measurements to be $\sim \pm 0.001$, but the level of accuracy of ⁸⁷Rb/⁸⁶Sr ratio measurements is more difficult to assess. We do not find evidence for large disturbance in ⁸⁷Rb-⁸⁷Sr systematics in K-rich feldspars,



Fig. 11 $^{87}\text{Rb}-^{87}\text{Sr}$ in situ isochron diagrams for Martian meteorite NWA 7034 (also known as Black Beauty). The $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{87}\text{Rb}/^{86}\text{Sr}$ ratios were corrected based on the ratio in the bracketing SRM610 standard. The $^{87}\text{Rb}/^{86}\text{Sr}$ ratio was further divided by 1.21 based on the Rb–Sr data acquired on the Shap granite (Fig. 7), following the approach of Bevan et al.⁵¹ The data points define an age 2190 \pm 60 Ma ($\pm 95\%$ CI) and an intercept of 0.7119 \pm 0.0017 ($\pm 95\%$ CI). The age and intercept do not change significantly when the three most radiogenic spot analyses are excluded from the regression (2235 \pm 72 Ma and 0.71148 \pm 0.00170, respectively). The same data corrected using the FGH glass standard and a secondary normalization using the Shap granite give an age and intercept of 2347 \pm 61 Ma and 0.7107 \pm 0.0023 (not shown), which are close to the values calculated from SRM610 + Shap. The high Rb/Sr spots in Black Beauty are alkali-rich feldspars.

as had been seen before by Nyquist *et al.*⁷⁹ in plagioclase. A possible explanation for this discrepancy could be a difference in the closure temperatures of plagioclase and K-rich feldspars.

Of the 108 laser spots analyzed, 30 have ${}^{87}\text{Rb}/{}^{86}\text{Sr} > 1$ and well resolved excesses in their 87Sr/86Sr ratios. We examined the section using an SEM after laser ablation analysis to (i) measure the K₂O/CaO in the laser ablation pits (Fig. 10) and (ii) estimate the grain size and petrographic context (Fig. S1⁺). The 30 high-Rb/ Sr spots were measured on 13 distinct grains as some larger grains were measured multiple times. The surface area of the grains was calculated based on SEM imaging, allowing us to compute equivalent diameters ($\emptyset = 2\sqrt{S/\pi}$ with S the surface area). The grains range in equivalent diameter between 111 and 460 µm. We calculated model ages for each grain by taking the slope of the lines defined by individual data points and the all-points isochron intercept (eqn (22) and (23)). This allows us to test if smaller grains have been more easily disturbed and give a different age than larger grains. We plot in Fig. 12 the 2-point model age for each spot against the diameter of the target grain. As shown, there is no relationship between the two and the data define a slope dt/da = -1.6 ± 2.2 Ma μm^{-1} (a is the radius in μm) that is indistinguishable from 0. Individual spot analyses are consistent with an 87 Rb– 87 Sr age of \sim 2.2 Ga and there is no indication of resetting at 1.4 Ga even for the smaller grains. Lindsay et al.81 calculated the temperature-time conditions needed for radiogenic ⁴⁰Ar to be lost and ⁴⁰Ar/³⁹Ar ages to be reset at 1.4 Ga in K-rich feldspar. Their estimate that heating was short-lived, ranging between ~ 5 h at 1000 °C and 10 year at 500 °C is likely to be a minimum as they did not account for the discrete distribution of diffusion domain sizes apparent in the degassing of virtually all their samples. We can estimate the effect that such heating events would have on Sr isotopes by modeling diffusive Sr isotope exchange between the interior of feldspar grains containing radiogenic ⁸⁷Sr and the surrounding medium. For each grain, we model that process as



Fig. 12 Two-point model ⁸⁷Rb–⁸⁷Sr age for individual K-feldspar Rbrich grains (eqn (22) and (23)) as a function of grain size (equivalent diameter). The solid horizontal line is the isochron calculated using all *in situ* data (~2.2 Ga; Fig. 11), while the dashed horizontal line is the ⁴⁰Ar/³⁹Ar plateau age obtained for K-rich grains by Lindsay *et al.*⁸¹ As shown, the grains show no obvious sign of resetting at 1.4 Ga.

diffusion in a sphere starting with uniform composition, with the composition at its surface kept at a constant value set by the surrounding medium. All nonradiogenic Sr isotopes are assumed to remain unchanged during the transient heating event. The equation governing the evolution of the ⁸⁷Sr/⁸⁶Sr ratio in the grain with time is,⁸⁴

$$\binom{^{87}\mathrm{Sr}}{^{86}\mathrm{Sr}}_{t_{\mathrm{h}}+\Delta t} = \binom{^{87}\mathrm{Sr}}{^{86}\mathrm{Sr}}_{t_{\mathrm{h}}} + \left[\binom{^{87}\mathrm{Sr}}{^{86}\mathrm{Sr}}_{b,t_{\mathrm{h}}} - \binom{^{87}\mathrm{Sr}}{^{86}\mathrm{Sr}}_{t_{\mathrm{h}}}\right]$$
$$\left[1 - \frac{6}{\pi^{2}}\sum_{n=1}^{\infty}\frac{1}{n^{2}}\exp\left(-\frac{Dn^{2}\pi^{2}\Delta t}{a^{2}}\right)\right], \quad (35)$$

where $\binom{87}{5} r^{86} Sr_{t_{+}+\Delta t}$, $\binom{87}{5} Sr_{t_{-}}^{86} Sr_{t_{-}}$, and $\binom{87}{5} Sr_{b,t_{+}}^{86} Sr_{b,t_{+}}$ are the Sr isotopic compositions in the grain (i) after the heating event, which lasted a time Δt , (ii) right before the heating event, and (iii) of the surrounding medium (bulk), a is the grain radius and D is the diffusivity. Strontium self-diffusion experiments give the temperature dependence of the diffusivity: $D = D_0 e^{-E/(RT)}$, with *R* the gas constant (8.3145 J K⁻¹ mol⁻¹), $D_0 = 10 \ \mu m^2 \ s^{-1}$ and $E = 167\ 000\ \text{J}\ \text{mol}^{-1}$.⁸⁵ We use the diffusivity measured by Giletti et al.85 rather than the one measured by Cherniak and Watson,⁸⁶ as the former were self-diffusion experiments relying on Sr isotopic analyses as opposed to chemical diffusion. Selfdiffusion data should be more relevant to the ⁸⁷Rb-⁸⁷Sr resetting scenario investigated here. We calculate below how the heating event that reset the ${}^{40}\text{Ar}/{}^{39}\text{Ar}$ system at a time $t_{\rm h}$ before present, could have influenced the isochron relationship if the Sr isotopic compositions of the grains were partially equilibrated with the surrounding medium but the Rb/Sr remained unaffected.

Knowing present ⁸⁷Rb/⁸⁶Sr and ⁸⁷Sr/⁸⁶Sr ratios measured in the grains and the bulk meteorite at present (subscript p), we can calculate the ⁸⁷Sr/⁸⁶Sr ratios at the time of the heating event, (⁸⁷Sr/⁸⁶Sr)_{t_h} = (⁸⁷Sr/⁸⁶Sr)_p + (⁸⁷Rb/⁸⁶Sr)_p(1 - e^{λt_h}). For example, the present bulk rock ⁸⁷Rb/⁸⁶Sr and ⁸⁷Sr/⁸⁶Sr ratios of NWA 7034 are 0.4275 and 0.726229, respectively,⁷⁰ corresponding to a bulk (⁸⁷Sr/⁸⁶Sr)_b ratio of 0.717784 at 1.4 Ga. The same calculation can be done to estimate (⁸⁷Sr/⁸⁶Sr)_i for each grain. We can then use eqn (35) to calculate how the thermal event could have partially reset the Sr isotopic composition of the grain to a new value (⁸⁷Sr/⁸⁶Sr)_{Δt}. We then calculate what the present Sr isotopic composition would be if the system had been disturbed but the ⁸⁷Rb/⁸⁶Sr ratio had not changed. The present ⁸⁷Sr/⁸⁶Sr isotopic composition of a grain disturbed at t_h would be,

$$\begin{pmatrix}
^{87}Sr\\ \overline{^{86}Sr}
\end{pmatrix}_{p}^{*} = \begin{pmatrix}
^{87}Sr\\ \overline{^{86}Sr}
\end{pmatrix}_{p} + \left\{ \begin{pmatrix}
^{87}Sr\\ \overline{^{86}Sr}
\end{pmatrix}_{b,p} - \begin{pmatrix}
^{87}Sr\\ \overline{^{86}Sr}
\end{pmatrix}_{p} + \left[\begin{pmatrix}
^{87}Rb\\ \overline{^{86}Sr}
\end{pmatrix}_{b,p} - \begin{pmatrix}
^{87}Rb\\ \overline{^{86}Sr}
\end{pmatrix}_{p} \right] (1 - e^{\lambda t_{h}}) \right\} \\
\left[1 - \frac{6}{\pi^{2}} \sum_{n=1}^{\infty} \frac{1}{n^{2}} \exp\left(-\frac{Dn^{2}\pi^{2}\Delta t}{a^{2}}\right) \right].$$
(36)

We used this formula to calculate the shift in 87 Sr/ 86 Sr associated with heating for 5 h at 1000 °C, or for 10 year at 500 °C. In both cases, the effect is negligible for all Rb-rich grains analyzed here. Available data therefore suggests that the thermal event that reset 40 Ar/ 39 Ar systematics did not reset 87 Rb- 87 Sr. Most likely, the 87 Rb- 87 Sr age of \sim 2.2 Ga (Fig. 11) represents the lithification time for the breccia and the 40 Ar/ 39 Ar system was reset by a later impact event.

This example shows that in situ ⁸⁷Rb-⁸⁷Sr analysis by LA-MC-ICP-MS/MS could be well suited to date samples that will hopefully be returned to Earth from Mars' Jezero crater around 2033.87,88 The Perseverance rover has identified a possible microgabbro in the Cf-fr (Crater floor-fractured rough) or Máaz formation on the floor of the Jezero crater.89 This rock shares similarities with differentiated basaltic martian meteorite Los Angeles,⁹⁰ which was dated using ⁸⁷Rb-⁸⁷Sr.⁹¹ It is therefore likely that some rocks returned from the Jezero crater will be datable by LA-MC-ICP-MS/MS. The MMX mission will return samples from Mars' moon Phobos in 2029.92,93 Spectroscopic observations hint at the presence of phyllosilicate and feldspar at the surface of Phobos,94 which could possibly be dated by LA-MC-ICP-MS/MS. The surface of Phobos could also contain fragments ejected from Mars95 that might be datable by LA-MC-ICP-MS/MS. Use of LA-MC-ICP-MS/MS rather than TIMS for ⁸⁷Rb–⁸⁷Sr analyses of returned samples will limit sample consumption and enable studies of minerals or fragments with different ages and geological histories.

4.2. Magma sources in the 26.5 ka Oruanui supereruption

The 26.5 ka Oruanui supereruption was the largest eruption to occur at Taupo Volcano in New Zealand, releasing 530 km³ of primarily rhyolitic magma in a period of weeks to months.96 It has been the subject of numerous studies aimed at understanding how such a large volume of differentiated magma could form, examining the roles of magmatic differentiation, partial melting, and assimilation. Based on ⁸⁷Sr/⁸⁶Sr ratio analyses of plagioclase crystals, Charlier et al.11 showed that the Oruanui magma body had a complex history. Through micromilling, they studied a plagioclase population characterized by the presence of rutile-rich cloudy cores. The crystal fraction of pumice clasts is $\sim 10\%$, $\sim 2/3$ of which are plagioclase. Among those plagioclase crystals, ~3% contain sub-rounded bluishgrey cloudy cores. While these crystals represent a small portion of the total volume of magma erupted ($\sim 0.2\%$), they are ubiquitous and bear witness of the processes of magma differentiation and crystal inheritance in the Oruanui magma body. These crystals contain three zones:¹¹ (i) a cloudy core (c) characterized by variable and elevated anorthite (An) content and slightly elevated ⁸⁷Sr/⁸⁶Sr (~0.7055–0.7065) relative to the bulk rocks, (ii) an overgrowth rim (o) with significantly higher An content and often more radiogenic ⁸⁷Sr/⁸⁶Sr reaching ~0.7076, and (iii) a euhedral rim (e) with an An content that decreases outwards to bulk rock values and a 87Sr/86Sr ratio that also decreases outwards from radiogenic to bulk rock values. The age of the samples and their low Rb/Sr ratios mean that the variations in ⁸⁷Sr/⁸⁶Sr are not due to *in situ* ⁸⁷Rb decay but rather



Fig. 13 *In situ* Sr isotopic analysis of a cloudy core (A and B) and a clear (D) plagioclase grains from the 26.5 ka Oruanui eruption, New Zealand. Similar grains were previously studied by Charlier *et al.*¹¹ using micromilling followed by TIMS isotopic analysis. c, o, and e in the various panels correspond to cloudy core, overgrowth rim, and euhedral rim, respectively. The cloudy core in (A) and (B) contains exsolved rutile. The overgrowth rim has higher An content than the euhedral rim and much of the cloudy core (E). Two transects measured across the cloudy feldpar (t3– t4 in panel (F) and t5–t6 in panel (G)) give ⁸⁷Sr/⁸⁶Sr isotopic compositions that are almost uniform but in detail, the ⁸⁷Sr/⁸⁶Sr ratio of the cloudy core seems to be more tightly clustered than the overgrowth and euhedral rims, which extend to more radiogenic values (IC) PDF stands for probability density function, calculated using a kernel density estimate). The clear feldspar grain has uniform ⁸⁷Sr/⁸⁶Sr isotopic composition (H). The grey bars in (C), (F), and (H) represents the range of ⁸⁷Sr/⁸⁶Sr values determined from individual pumice clasts in the Oruanui rhyolite.¹¹² Given the young ages and relatively low ⁸⁷Rb/⁸⁶Sr ratios of the grains, radiogenic ingrowth of ⁸⁷Sr after eruption can be neglected.

reflect the contributions of three different magma sources. The cloudy core, overgrowth rim, and euhedral rim are thought to be derived from assimilation of intermediate-composition crustal rocks, melts produced by melting of ancient greywacke basement, and bulk rock magma composition, respectively.¹¹ Measurement of micromilled samples by TIMS is time

Paper

consuming, limiting the number of analyses that can be performed. The precision achieved on ⁸⁷Sr/⁸⁶Sr isotopic analyses by Charlier *et al.*¹¹ is on the order of $\sim \pm 0.0001$, which is more than sufficient to detect 0.7055-0.7076 (~0.0020 span) variations in ⁸⁷Sr/⁸⁶Sr ratios. With LA-MC-ICP-MS/MS on the same samples, we achieved precisions of $\sim \pm 0.0007$ on 100 μ m spots, which is worse than TIMS but is still more than sufficient to resolve the isotopic variations previously documented, especially given that many laser spots can be measured on a single sample, which can help improve statistics. We have analyzed several transects along two single plagioclase crystals (a cloudy core grain and a clear grain) from the 26.5 ka Oruanui supereruption (Fig. 13). The cloudy core grain shows the same An profile as those previously documented by Charlier et al.11 The 87Sr/86Sr ratio shows limited variation, but this could be a matter of grain selection as previous data showed significant grain-to-grain variability. In the grain that we analyzed, the cloudy core has an 87 Sr/ 86 Sr ratio that is close to the bulk rock value (~0.7054), while the overgrowth and euhedral rims extend to more radiogenic values of around (~ 0.7060). This is not readily visible when plotting the two transects on the cloudy core grain individually, as one transect contains mostly cloudy core data points (t3-t4; Fig. 13F), while the other contains primarily overgrowth rim data points (t5-t6; Fig. 13G). This is clearly seen, however when plotting the distribution of ⁸⁷Sr/⁸⁶Sr ratios in each zone in the form of a kernel density estimate (Fig. 13C). In the clear plagioclase grain, we see no resolvable 87Sr/86Sr variation (Fig. 13H). Overall, this study shows that while the precision of LA-MC-ICP-MS/MS is not as good as TIMS, which has a better useful yield than LA-MC-ICP-MS/MS for Sr (1.5% (ref. 97) vs. 0.25%), the precision is still sufficient to detect magma mixing and assimilation based on in situ ⁸⁷Sr/⁸⁶Sr isotopic analyses.

4.3. Meteoritic hibonite inclusions

Hibonite is a highly refractory mineral found as inclusions in primitive meteorites (nominally CaAl₁₂O₁₉ but with some minor element substitutions, predominantly $2Al^{3+} \leftrightarrow Mg^{2+} + Ti^{4+}$), notably in the CM carbonaceous chondrite group.98-100 These hibonite inclusions are classified into several subgroups depending on their morphologies and mineral associations (PLAty-hibonite Crystals = PLACs, Spinel-HIBonite inclusions = SHIBs, Blue AGgregates = BAGs). Hibonite inclusions have unusual isotopic traits among meteoritic materials. Those of the PLACs variety often display large ⁴⁸Ca and ⁵⁰Ti anomalies, yet did not incorporate any of the short-lived nuclide ²⁶Al ($t_{1/2}$ = 0.7 Ma).98,101-105 SHIBs are less exotic in their compositions and are more akin to large refractory inclusions also found in some carbonaceous chondrites, with absent or more subdued isotopic anomalies and near canonical initial ²⁶Al/²⁷Al ratio of 5 \times 10⁻⁵.^{98,101,104,106,107} We analyzed the Sr isotopic composition of seven hibonite-rich and spinel-hibonite inclusions that were separated from the CM2 chondrite Murchison and were previously investigated for their O, Ti, and Ca isotopic compositions as well as ²⁶Al-²⁶Mg systematics.^{105,106} They range in size between ${\sim}40$ and 100 μm and comprise 5 PLAC-like samples and 2 SHIBs. All the 5 PLAC-like samples have nondetectable



Fig. 14 87 Sr/ 86 Sr isotopic compositions of hibonite inclusions extracted from the Murchison CM carbonaceous chondrite. The solid horizontal line is the solar system initial value (0.69876 \pm 0.00002 (ref. 109) 0.69883 \pm 0.00002 (ref. 110)). Hibonite inclusions are ultrarefractory and formed at the birth of the solar system with very low Rb/Sr. As expected, we find that they have 87 Sr/ 86 Sr ratios close to the solar system initial. The slightly more radiogenic compositions in some of them are most likely due to incorporation of Rb from the matrix of Murchison.

initial ²⁶Al/²⁷Al ratios, consistent with their formation either (i) early in a region of the solar nebula that had not incorporated ²⁶Al, or (ii) less likely late after ²⁶Al-decay. Most samples have normal (near-terrestrial) ⁴⁸Ca and ⁵⁰Ti isotopic compositions except for one (HIB1-5-3) that shows anomalous deficits for these isotopes of $\sim -0.4\%$ (40 ϵ -units).¹⁰⁵ PLACs and SHIBs contain $\sim 20-100$ and 50-200 ppm Sr, respectively^{99,100} and are devoid of Rb. Our motivation for measuring the Sr isotopic compositions of hibonite inclusions was to search for possible isotopic anomalies¹⁰⁸ and compare the ⁸⁷Sr/⁸⁶Sr ratios with the known solar system initial ratio (0.69876 \pm 0.00002;¹⁰⁹ 0.69883 \pm 0.00002;¹¹⁰ 0.698784 \pm 0.000076 (ref. 97)). Given the small size and refractory nature of hibonite inclusions, we changed the laser beam spot to 35 µm and the repetition rate to 12 Hz. The signal remained approximately constant during the ablation, suggesting that the laser did not couple well with the sample and no laser-spot deepening effect happened. All hibonite inclusions have ⁸⁷Sr/⁸⁶Sr ratios close to the solar system initial (Fig. 14). Platy hibonite HIB1-5-3, which has 0.4% excesses in ⁴⁸Ca and ⁵⁰Ti has a 1.4% excess in ⁸⁷Sr relative to the solar initial. Similar ⁸⁷Sr excesses are found in other hibonite grains with normal ⁴⁸Ca and ⁵⁰Ti. Examination of the BSE image of HIB1-5-3 shows that it is somewhat porous and appears to have some Rb-bearing Murchison matrix in the pores, which might explain its high ⁸⁷Sr/⁸⁶Sr ratio. The 1.4% ⁸⁷Sr excess in HIB1-5-3 is therefore unlikely to be of nucleosynthetic origin.

5. Conclusion

We present methodologies for *in situ* analysis and reduction of ⁸⁷Rb–⁸⁷Sr data acquired by LA-MC-ICP-MS/MS. The use of a double Wien mass filter combined with fluorination in a hexapole collision/reaction cell make it possible to measure ⁸⁷Sr/⁸⁶Sr ratios in samples with elevated ⁸⁷Rb/⁸⁷Sr ratios. Laser ablation data reduction is done with a Mathematica-based graphical user interface software named LASr. Instrumental fractionation is dealt with by bracketing sample by standard

measurements. We derive formulas to propagate all uncertainties and their correlations for ⁸⁷Rb/⁸⁶Sr and ⁸⁷Sr/⁸⁶Sr ratios. We have measured several standards (Durango apatite, SRM610, SRM612, feldspar glasses) to show that the data were accurate. Measurement uncertainty calculated from repeat laser ablation data agrees with expectations for Johnson noise and counting statistics. For the same amount of Sr consumed, the data generated by LA-MC-ICP-MS/MS are less precise than those obtainable by TIMS, but the measurements are less destructive and sample throughput is higher. LA-MC-ICP-MS/MS is thus very well suited to analyze small and precious samples, to tackle questions that require knowledge and preservation of petrographic context, and to examine population characteristics. We have used the Neoma MS/MS on several applications to showcase its unique capabilities. We present in situ ⁸⁷Rb-⁸⁷Sr data of the Martian polymict breccia NWA 7034 (Black Beauty) that resolve a long-standing problem in the chronology of this sample. We show that K-rich feldspar define a clear 2.2 Ga age, which most likely reflects the age of lithification for this sample. The younger 1.4 Ga 40 Ar/39 Ar ages most likely reflect later resetting by an impact that was too short-lived or did not reach a sufficient temperature to reset the ⁸⁷Rb-⁸⁷Sr chronometer. This result demonstrates the usefulness of this technique for dating precious extraterrestrial samples, such as the ones that will be collected from Phobos by the MMX mission,^{92,93} or those that are now being collected by the Perseverance rover on Mars in the Jezero crater.87,88

Conflicts of interest

The authors declare the following competing financial interest(s): Dr Grant Craig, Dr Claudia Bouman, Dr Nicholas Lloyd, Dr Darren Tollstrup, Dr Johannes Schwieters are employed by Thermo Fisher Scientific (Bremen) GmbH.

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