DEVELOPING HIGH PRECISION IN-SITU RB-SR ISOTOPIC ANALYSES BY FEMTOSECOND LASER ABLATION MC-ICPMS/MS. H. Melton[1], T. E. Yap[1], A.M. Cruz-Uribe[2], F.L.H. Tissot[1], [1]The Isotoparium, Geological & Planetary Sciences Div., Caltech, Pasadena, CA 91125, USA (hmelton@caltech.edu, tyap@caltech.edu), [2]School of Earth and Climate Sciences, University of Maine, Orono, ME 04469, USA.

Introduction: The Rb-Sr beta-decay system has been a workhorse of geochronology and geoforensics, widely applied to terrestrial, lunar, and Martian specimens [1,2,3]. This radiometric dating system exploits the chemical similarities (*i.e.,* same valency, similar ionic radii) between Rb (Sr) and K (Ca), the latter being common rock-forming elements. Using minerals with a spread in Rb/Sr ratios, an isochron can be constructed from which the sample's Rb-Sr date (*e.g.,* its crystallization age) and initial $^{87}Sr/^{86}Sr$ ratio can be calculated.

One main limitation of the Rb-Sr system is the need for complete sample digestion followed by time- and labor-intensive chemistry to separate Rb and Sr due to the ^{87}Rb-^{87}Sr isobaric interference before measurement on a thermal ionization mass spectrometer (TIMS) [4]. In-situ approaches to Rb-Sr measurements have long attracted interest, with recent techniques using laser ablation (LA) and some form of a gas reaction cell [5] to separate Rb and Sr ions on-line and achieve comparable precision to solution work. The desire for an in-situ approach helped to drive instrumentation development, including the Proteus instrument, which demonstrated in-situ Rb-Sr isochron measurements with a LA-coupled, multicollector inductively coupled plasma tandem mass spectrometer (MC-ICPMS/MS) with a collision cell and quadrupole pre-cell mass filter [6]. The next generation of this instrument, the Neoma, features a dual Wien pre-cell mass filter, and yields high-precision Rb-Sr measurements across a host of geologic material, including K-feldspar grains in the Martian meteorite Northwest Africa 7034 (Black Beauty) and single-spot analysis of metamorphic biotite leveraging the spatial accuracy of the LA system [7,8].

Previously, high-precision LA measurements mostly relying on nano-second (ns) pulse widths have suffered from both isotopic and elemental fractionation during ablation, which newer generations of femtosecond (fs) lasers promise to solve with their extremely short, high intensity pulses [9-10]. Here we describe the method development coupling a fs-LA system and the Neoma MS/MS for Rb-Sr isotopic analyses, and explore its behavior with several well-characterized glass reference materials.

Methods and Samples: This method utilizes an ESL NWRFemto 257nm fs-LA system coupled to a Thermo Fisher Scientific™ Neoma MC-ICPMS/MS with a collision-reaction cell (CRC) and a pre-cell dual Wien mass filter. The filter uses perpendicular electric (E) and magnetic (B) fields to deflect the incoming ions

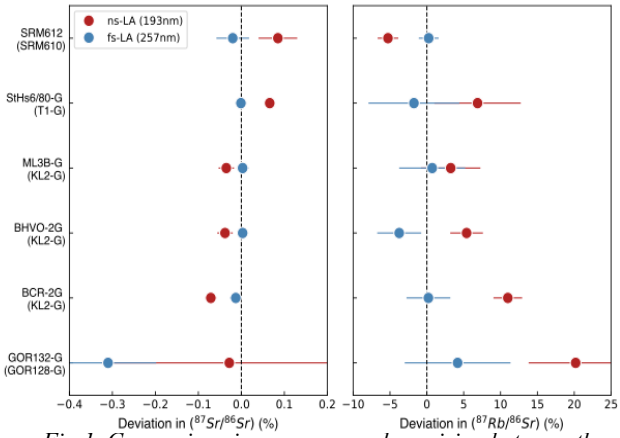

Fig 1. Comparison in accuracy and precision between the 257nm fs-LA system used in this work and previous results from a 193nm ns-LA system [11]. The bracketing standard for each sample is given in parentheses.

based on their *m/z* ratio before isolating the desired mass band with a physical slit. It then re-collimates the beam before entry into the CRC. To separate the Sr from the Rb on-line, a mixture of ultrapure 95 % helium carrier gas and 5 % SF_6 reaction gas was introduced into the CRC, fluorinating the incoming Sr ions and mass-shifting them heavier by ~19 *m/z* while leaving the Rb ions essentially unreacted. With sample-standard bracketing, this allows for independent measurement of Rb and Sr isotopes without the need for peak stripping, but requires the mass range that Sr is shifted to (103-107 amu) to be free of interferences (*e.g.,* ^{103}Rd, ^{106}Pd, ^{107}Ag). To ensure that this is the case, the pre-cell mass filter is tuned to only allow through the ~82 to 100 amu mass range, passing Rb and Sr ions while rejecting all others. This is an iterative process on the Neoma MS/MS involving tuning the pre-cell filter E and B fields as well as the hexapole CRC lenses and gas flows. Care must be taken to avoid interferences created by the SF_6 gas itself on ^{88}SrF (SF_3OH_2) and ^{86}SrF (SF_3O), but these interferences are resolvable on low resolution mode. The laser was found to give a good balance of signal intensity, precision, and measurement time at a scan speed of 10 µm/s, a line length of 400 µm, a firing repetition rate of 40 Hz, an energy of 55 % (resulting in fluence of ~ 3 J cm^{-2}), and He sample gas flow of ~900 mL/min, and unless otherwise noted these parameters were used for all measurements.

A variety of reference glasses from NIST, MPI-DING, and USGS were analyzed. These glasses have a wide range of Rb and Sr concentrations (~2 to 400 ppm

and ~15-500 ppm, respectively), $^{87}Sr/^{86}Sr$ isotopic compositions (0.703469 to 0.710137), and matrix major element compositions.

Results: *Precision and accuracy; femto- vs. nanosecond.* As shown in Fig.1, our method produces high-quality isotopic and elemental data compared to literature data obtained with a 193nm ns-LA system, also coupled to a Neoma MS/MS [11]. The $^{87}Sr/^{86}Sr$ isotopic compositions are measured with accuracies exceeding 0.03 % (deviation from TIMS-derived value) and 2SE precisions of ~1 ‰, and the $^{87}Rb/^{86}Sr$ ratio with accuracies within 5 % and 2SE precisions of ~3 %. There are some notable exceptions – in the last line of Figure 1, the measurement of $^{87}Sr/^{86}Sr$ and $^{87}Rb/^{86}Sr$ ratios in GOR132-G bracketed by GOR128-G is inaccurate by ~0.3 % and ~5 % respectively, likely due to low Sr concentrations.

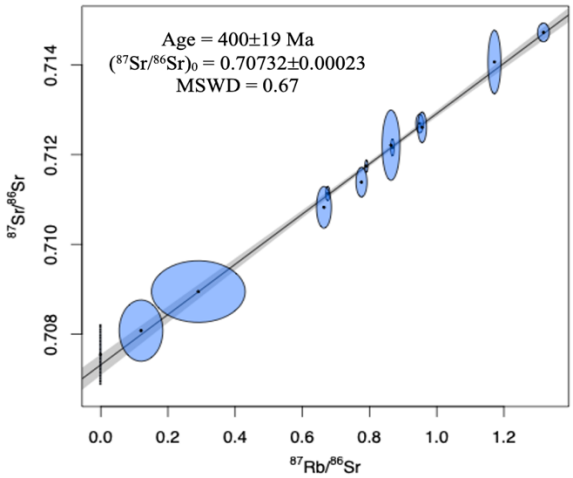

Fig 2. Isochron from a sample of the Shap Granite.

Shap Granite Isochron. A sample of the Shap Granite was used to test the accuracy of isochrons created using this method (Fig. 2). The measured isochron has a calculated age of 400±19 Ma, aligning well with the reported value of 405±2 Ma [12].

Parameter Sweep: $^{87}Rb/^{86}Sr$ accuracy deviation. While the results in Fig. 1-2 are promising, there is still a surprising amount of (sample standard differential) elemental fractionation for a fs laser, and so a sweep of the laser parameters was conducted. By only changing the pulse energy and the repetition rate, the $^{87}Rb/^{86}Sr$ ratio can be altered significantly (few % offset). There is little structure to these results, indicating that there may be several yet unidentified confounding variables.

Fluorination Reaction Efficiency. One such potential variable is the fluorination reaction efficiency – by using sample-standard bracketing, the effects of an unideal reaction efficiency can be cancelled to the first order. This relies on a constant reaction efficiency, however, and so an intensity mismatch test was conducted. By bracketing NIST610 with itself and varying the repetition rate of the laser, the mass load going into the

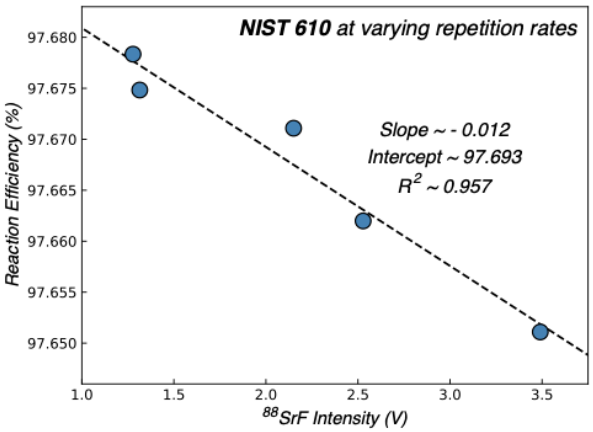

Fig 3. Effect of mass load on fluorination reaction efficiency, using the measured ^{88}SrF voltage as a proxy for mass load and NIST610 bracketed by itself as the sample. The intensity was varied by changing the repetition rate.

CRC was changed. As seen in Fig. 3, there is a clear trend towards lower reaction efficiency at higher signal intensities, possibly corresponding to a dynamic, local depletion of SF_6 in the CRC beampath. This effect is relatively small, though, and would only account for <0.2 % inaccuracy of the $^{87}Rb/^{86}Sr$ ratio, but indicates that the sample and standards should be intensity matched for best results.

Discussion: The method described here produces high-precision Rb-Sr isotopic data, but particularly with a fs-LA system, there should be minimal elemental fractionation, and so further testing must be conducted. We also plan similar work regarding a method for single-spot analyses. The development of this method is done in anticipation for Mars Sample Return. Indeed, the Perseverance rover has identified lithologies in the Maáz formation of Jezero crater that appear to be good candidates for in-situ Rb-Sr analysis, but this method is widely applicable.

References: [1] Papanastassiou D.A. & Wasserburg G.J. (1970) *EPSL, 8,* 269-278. [2] Jäger E. & Hunziker J.C. (1979) *Lectures in Isotope Geology,* 13-26. [3] Borg L.E. et al. (1999) *Science, 286,* 90-94. [4] Vanhaecke F. et al. (2001) *Fresenius J. Anal. Chem., 371,* 915-920. [5] Zack T. & Hogmalm K.J. (2016) *Chem. Geol., 437,* 120-133. [6] Bevan D. et al. (2021) *JAAS, 36,* 917-931. [7] Dauphas N. et al. (2022) *JAAS, 37,* 2420-2441. [8] Cruz-Uribe A.M. et al. (2023) *Geostand. Geoanalytical Res., 47,* 795-809. [9] Ingo, H. and F. Von Blanckenburg (2007) *Spectro. Acta Part B, 62,* 410-422. [10] Poitrasson F. & d'Abzac F.X. (2017) *JAAS., 32,* 1075-1091. [11] Cruz-Uribe A. et al. (2023) Thermo Fisher Sci. Application Note 002246. [12] Davidson J. et al. (2005) *Geology, 33,* 29-32.