Dating the Martian meteorite Zagami by the $^{87}$Rb-$^{87}$Sr isochron method with a prototype in situ resonance ionization mass spectrometer

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RATIONALITY: The geologic history of the Solar System builds on an extensive record of impact flux models, crater counts, and ~270 kg of lunar samples analyzed in terrestrial laboratories. However, estimates of impactor flux may be biased by the fact that most of the dated Apollo samples were only tenuously connected to an assumed geologic context. Moreover, uncertainties in the modeled cratering rates are significant enough to lead to estimated errors for dates on Mars and the Moon of ~1 Ga. Given the great cost of sample return missions, combined with the need to sample multiple terrains on multiple planets, we have developed a prototype instrument that can be used for in situ dating to better constrain the age of planetary samples.

METHODS: We demonstrate the first use of laser ablation resonance ionization mass spectrometry for $^{87}$Rb-$^{87}$Sr isochron dating of geological specimens. The demands of accuracy and precision have required us to meet challenges including the regulation of the ambient temperature, measurement of appropriate backgrounds, sufficient ablation laser intensity, avoidance of the defocusing effect of the plasma created by ablation pulses, and shielding of our detector from atoms and ions of other elements.

RESULTS: To test whether we could meaningfully date planetary materials, we have analyzed a piece of the Martian meteorite Zagami. In each of four separate measurements we obtained $^{87}$Rb-$^{87}$Sr isochron ages for Zagami consistent with its published age, and, in both of two measurements that reached completion, we obtained better than 200 Ma precision. Combining all our data into a single isochron with 581 spot analyses gives an $^{87}$Rb-$^{87}$Sr age for this specimen of 360 ±90 Ma.

CONCLUSIONS: Our analyses of the Zagami meteorite represent the first successful application of resonance ionization mass spectrometry to isochron geochronology. Furthermore, the technique is miniaturizable for spaceflight and in situ dating on other planetary bodies. © 2014 The Authors. Rapid Communications in Mass Spectrometry published by John Wiley & Sons Ltd.
extrapolations can result in errors in the modern impact rate of up to a factor of 4, as illustrated by the formation rate of new craters observed on Mars over the last decade by the High Resolution Imaging Science Experiment (HiRISE) instrument.\(^\text{[19]}\)

Although the technology exists to radioisotopically date fragments of other planetary bodies that have come to Earth as meteorites, these specimens arrive bereft of geological context from their locations of origin (e.g.,\(^\text{[20]}\)). Hence, it has long been an interest of planetary scientists to determine ages of planetary samples in situ, on the surface of another planet. Here we use the term “in situ” in the sense of “in the field”, rather than merely implying that the rock is examined without disaggregating or separating the minerals from their petrographic context. The alternative to in situ dating of planetary materials is the return of carefully contextualized samples to Earth. While this is very desirable for the number and precision of laboratory techniques that could be engaged, there can be no doubt of the high cost, technical challenge, and time needed for a sample return mission. For this reason, the National Research Council Decadal Survey recommended continuing development of in situ geochronology techniques,\(^\text{[21]}\) and a capability goal of ±200 Ma for the NASA Technology Roadmap was established.\(^\text{[12]}\) Even in the context of a sample return mission, in situ dating can be a valuable tool for identifying the most scientifically rewarding samples to collect for more detailed analysis back on Earth.

Most of the leading geochronological techniques, such as thermal ionization mass spectrometry (TIMS), ion microprobe analysis, laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS), and noble gas mass spectrometry, have long been thought to be impossible to implement on planetary missions. Often, the demand for extreme sensitivity and high precision imposes requirements for large mass, volume, or power that are impractical for spacecraft. In other cases, samples must be hand-processed to avoid isobars that would otherwise interfere with the dating isotopes. In addition, all age determinations require isotopic measurements to be complemented by analyses that provide context and assess the presence and extent of secondary alteration.

Despite these issues, several groups have suggested approaches for in situ dating, especially with applicability to specimens collected on Mars.\(^\text{[23–26]}\) These proposals use either the \(^{40}\text{K}-^{40}\text{Ar}\) or the \(^{87}\text{Rb}-^{87}\text{Sr}\) isotopic systems. Although K is much more abundant than Rb in Martian meteorites,\(^\text{[30]}\) the fact that \(^{40}\text{K}\) is only ~0.01% of natural K means that the radioactive isotopes \(^{40}\text{K}\) and \(^{87}\text{Rb}\) (as well as \(^{147}\text{Sm}\), \(^{232}\text{Th}\), and \(^{238}\text{U}\)) are of comparable abundance. A review in 2012 of the dating techniques applied to meteorites listed in the Mars Meteorite Compendium\(^\text{[27,31]}\) reveals that 28% were dated with \(^{87}\text{Rb}-^{87}\text{Sr}\) and 8% with \(^{40}\text{K}-^{40}\text{Ar}\); 85% of the \(^{87}\text{Rb}-^{87}\text{Sr}\) measurements were concordant with an independent technique. The various techniques lend themselves to certain isotopic systems but not others. For example, laser-induced breakdown spectroscopy can detect K at its likely concentrations on Mars, but is insufficiently sensitive to measure Rb and Sr isotopes at concentrations found in SNC meteorites.\(^\text{[32]}\) Resonance ionization mass spectrometry can selectively ionize Rb and Sr, but cannot do so for Ar because its electronic transitions are far into the ultraviolet. Nevertheless, resonance ionization is applicable to many elements (e.g.,\(^\text{[33]}\)), including other elements of interest for dating such as Pb-Pb and Sm-Nd, and our technique could be applied to these systems by using either tunable lasers or additional fixed-wavelength lasers.

The first radioisotopic age determination on another planetary body was accomplished by Farley et al.\(^\text{[34]}\) who analyzed bulk powdered samples of a mudstone from Gale Crater, Mars, with instruments aboard the Curiosity rover, and determined a \(^{40}\text{K}-^{40}\text{Ar}\) age of 4.21 ± 0.35 Ga. However, the validity of the quoted age depends critically on the assumption that all the \(^{36}\text{Ar}\) in the sample was produced by cosmic ray bombardment, with no \(^{36}\text{Ar}\) having come from the Martian atmosphere or mantle contamination, a known issue for SNC meteorites.\(^\text{[35–37]}\) If even ~5% of the \(^{36}\text{Ar}\) were atmospheric, the amount of atmospheric \(^{40}\text{Ar}\) then implied in the sample would yield an age nearly 1 Ga younger. The assumption of no atmospheric argon may be true in this case, but it is impossible to be sure on the basis of a total fusion experiment. Isochron experiments, by contrast, provide internal tests of the validity of an age by demonstrating whether a sample contains atoms of the daughter isotope in a binary mixture of radiogenic and inherited material. Furthermore, bulk measurements provide only limited assessment of petrographic relationships and potential alteration.

The use of laser ablation resonance ionization mass spectrometry for \(^{87}\text{Rb}-^{87}\text{Sr}\) geochronology was first suggested in 1994 and 1995\(^\text{[23,38]}\) and though the potential of the technique for in situ isotopic measurements was noted throughout the following decade,\(^\text{[25,39–43]}\) the measurement was never demonstrated due to difficulties in stabilizing the production of resonance ions.\(^\text{[23]}\) In this work we have overcome these difficulties to demonstrate, for the first time, the use of laser ablation resonance ionization mass spectrometry (LARIMS) for \(^{87}\text{Rb}-^{87}\text{Sr}\) geochronology, and we have analyzed the Martian meteorite Zagami, a sample directly relevant to planetary exploration.

**BACKGROUND**

The Zagami meteorite

The Martian basaltic shergottite Zagami has been dated using thermal ionization mass spectrometry measurements of mineral separates including pyroxenes, maskelynite, and oxides.\(^\text{[44]}\) Using the purest fine-grained mineral fractions, Borg et al.\(^\text{[44]}\) determined an \(^{87}\text{Rb}-^{87}\text{Sr}\) isochron age of 176 ± 2 Ma, and an initial \(^{87}\text{Sr}/^{86}\text{Sr}\) ratio of 0.72156 ± 0.00002. Among these mineral analyses, agreement of the isotopic data with a straight-line isochron was characterized by a mean square weighted deviation (MSWD) of 1.1. Borg et al.\(^\text{[44]}\) also defined a more “representative” isochron, using all the mineral separates, which implied an age of 166 ± 6 Ma and \((^{87}\text{Sr}/^{86}\text{Sr})_{\text{initial}} = 0.72157 ± 0.00008\). These data exhibited greater scatter from a straight line, with MSWD of 17. Other authors, using fine- and coarse-grained Zagami samples, have derived similar \(^{87}\text{Rb}-^{87}\text{Sr}\) ages of 183 ± 6 Ma\(^\text{[45]}\) and 180 ± 4 Ma\(^\text{[46]}\) and this age is thought by Borg et al.\(^\text{[44]}\) to represent the time of crystallization of the rock on Mars. For this experiment, we purchased a 0.313 g cut slab of the Zagami meteorite from the Meteorite Market.\(^\text{[47]}\) This sample was...
placed into a rectangular ‘stub’ of vacuum epoxy alongside a similarly sized cut slab of standard GSD-1G,[48,49] which were then roughly polished to keep the specimen surfaces co-planar.

Resonance ionization

Resonance ionization mass spectrometry[50] is an analytical technique that is advantageous for applications demanding high sensitivity or exceptional elemental selectivity. Briefly, electrically neutral atoms are liberated from a specimen (in our case by laser ablation), and the plume of vaporized atoms is then irradiated by pulsed lasers tuned to excite electronic resonances in the elements of interest.[33,53] The excited atoms are then ionized, usually by additional photons, and the resulting ions are accelerated into a time-of-flight mass spectrometer, which separates isotopes by mass. If the lasers are sufficiently intense, the laser excitation process can ionize nearly all the atoms of the elements of interest, so that atom yields are often limited only by the ion optics of the mass spectrometer (e.g.,[52]). Therefore, with high transmission mass spectrometers, it is possible to study the isotopic composition of even ultra-trace elements by this technique. For example, Trautmann et al.[53] analyzed the isotopic composition of 15-part-per-trillion plutonium in depleted uranium ammunition from the Balkans conflict of the 1990s, and dated the plutonium by measuring a deficit of short-lived 241Pu relative to recent weapons grade material. More recently, Strashnov and Gilmour[54] determined the cosmic ray exposure ages of individual milligram-sized chondrules from the Allagan meteorite, by measuring the abundances of krypton isotopes (after separating krypton from other elements by gettering and selective freezing) with detection limits of <100 atoms.

The high sensitivity of resonance ionization to elements of interest is matched by its high degree of insensitivity to atoms of other elements. This eliminates the need, in many applications, to perform extensive chemical separations of an element of interest. For example, Lugaro et al.[55] identified signatures of s-process nucleosynthesis among zirconium and molybdenum isotopes in presolar silicon carbide grains, which required the detection of each element without interference from the other at isotopic masses 92, 94, or 96, which they share. Likewise, Levine et al.[56] reported anomalous abundances of chromium isotopes in individual presolar grains, which required effective suppression of potentially interfering 54Ti and 54Fe. Chemical separation of the ppm-level elements analyzed by Lugaro et al.[55] and Levine et al.[56] from individual ~3 μm mineral grains is not practical, so the isotopic anomalies that they observed could not have been detected without the high elemental selectivity of the resonance ionization process.

In our experiment, the elemental selectivity of resonance ionization is particularly important. Rubidium-87 decays radioactively to stable 87Sr (half-life 49,624±65 μs[57]), but because the decay leaves the isotopic mass unchanged, dating experiments with this isotopic system must employ some means of separating Rb from Sr. To give a recent example, de Mayer et al.[58] used analyses of Rb and Sr from phengite micas both within and outside larger garnet crystals to assess the timing of garnet growth during metamorphism of eclogites from the Swiss Western Alps. They separated Rb from Sr by ion-exchange chromatography, and then measured the isotopic ratios of each element by thermal ionization mass spectrometry. Instead of chemically separating Rb from Sr, in our experiment we selectively ionize laser-ablated Sr and Rb at different times using resonance ionization. Typically, we photoionize Rb ~2 μs after Sr. Once ionized, the Sr and Rb are electrostatically accelerated into our time-of-flight mass spectrometer, so 87Rb ions arrive at the detector ~2 μs after 86Sr ions. With this delay of the Rb photoionization, we observe well-separated peaks corresponding to 86Sr, 87Sr, 88Sr, 85Rb, and 87Rb in our time-of-flight spectra (Fig. 1). A principal advantage of separation of isotopes by resonance ionization is that laser systems can be miniaturized for spaceflight (e.g.,[59]), so resonance ionization is a very attractive option for in situ dating of materials on other planetary bodies.[60]

We excite two single-photon resonant transitions and then non-resonantly photoionize each element (Fig. 2). For Rb, ground-state (i.e., [Kr]5s 2S1/2) atoms are excited by 780.24 nm radiation from an optical parametric oscillator to the [Kr]5p 2P1/2 state at 12,816 cm−1, then further promoted by 776.98 nm light from a dye laser to the [Kr]5d 1D2/2 state at 25,703 cm−1, and then finally ionized by light from a 1064 nm Nd:YAG laser (the ionization limit for Rb is 33,691 cm−1). For Sr, we excite atoms from the [Kr]5s2 1S0 ground state to the [Kr]5s5p 1P1 state at 21,698 cm−1 with 460.86 nm light from an optical parametric oscillator, excite them further with 554.49 nm radiation from a dye laser to the [Kr]5s6d 1D2 state at 39,733 cm−1, and finally ionize them with 1064 nm light from another Nd:YAG laser (the ionization limit for Sr is 776.98 nm from a dye laser to the [Kr]5s6d 1D2 state at 25,703 cm−1, and then finally ionized by light from a 1064 nm Nd:YAG laser (the ionization limit for Rb is 33,691 cm−1). For Sr, we excite atoms from the [Kr]5s2 1S0 ground state to the [Kr]5s5p 1P1 state at 21,698 cm−1 with 460.86 nm light from an optical parametric oscillator, excite them further with 554.49 nm radiation from a dye laser to the [Kr]5s6d 1D2 state at 39,733 cm−1, and finally ionize them with 1064 nm light from another Nd:YAG laser (the ionization limit for Sr is 776.98 nm from a dye laser to the [Kr]5s6d 1D2 state at 25,703 cm−1, and then finally ionized by light from a 1064 nm Nd:YAG laser (the ionization limit for Rb is 33,691 cm−1).

![Figure 1. Time-of-flight spectra for GSD-1G standard glass.](Image 475x748 to 494x767)

Lighter curve (offset downwards by 3 mV for clarity) is the mean of 2000 shots with second-step resonance lasers only, added to the mean of 2000 shots with first-step resonance and ionization lasers. Darker curve is the average of 2000 shots with all resonance lasers fired, showing peaks corresponding to the labeled Sr and Rb isotopes. Lighter curve (offset downwards by 3 mV for clarity) is the mean of 2000 shots with first-step resonance lasers only, added to the mean of 2000 shots with second-step resonance and ionization lasers. A small background under the 87Sr peak allows us to quantify how much of that peak is due to accidental ionization of other species (here, presumably molecules) with mass 87, rather than to strontium. For these shots, Rb ions were created 2.3 μs after the Sr ions; they arrive at the detector correspondingly later in spite of both elements having an isotope of mass 87.
Among the advantages of multiphoton processes is that we can quantitatively assess our unwanted backgrounds: by pulsing only the optical parametric oscillators that drive the first transitions in our resonance schemes, or only the dye lasers that drive the second transitions, and we can observe the extent of non-resonant ionization (which is undesirable because it need not be elementally specific) and any ionization due to accidental resonances with one of our lasers. In contrast to these sources of background, ionization of Rb and Sr requires the simultaneous pulsing of all the lasers driving the relevant transitions. We show background spectra in Fig. 1; the photoion signal produced by the lasers individually is very small compared with the photoion signal produced by the spatially and temporally overlapping lasers. Ions detected in the former case are unlikely to be Sr or Rb (and, indeed, we see that a weak molecular interference is present under the $^{87}$Sr peak), while the additional ions detected in the latter case almost certainly are.

We detect most isotopes of each element in approximately their natural proportions, but we more favorably detect Rb than Sr. For example, in the GSD-1G reference glass, strontium is more abundant than Rb by a factor of 1.86 yet in our analysis of this glass (Fig. 1), we detect 6.5 times more Rb than Sr (i.e., the elemental fractionation factor favoring Rb is ~12). This fractionation could arise easily from any of a number of physical causes, such as (a) more efficient thermal ablation of Rb; (b) more efficient resonance ionization of Rb, e.g., by ionizing Rb from a larger volume of the vaporized plume; (c) differences in the intensities of the resonance lasers for each element; or (d) differences in the speeds with which atoms of the two elements emerge from the sample surface. We monitor the elemental fractionation by analyzing standards at regular intervals during a run, so that we can ultimately correct our data for this effect.

We use the standard analyses to monitor isotopic fractionations as well, though most of these are small. The exception is the routine over-detection of $^{86}$Sr relative to other Sr isotopes, which presumably arises because of more efficient optical excitation of the odd isotope through excited states with multiple hyperfine sublevels. Such odd-even isotope effects are well known in resonance ionization spectroscopy (e.g.,), and we apply corrections for the fractionation of this (and all other) isotopic ratios based on our standard analyses.

**Figure 2.** Resonance ionization schemes employed to excite and ionize Rb and Sr. Atoms of these elements are excited by successive absorption of three photons (shown schematically as arrows) with indicated wavelengths, passing through two intermediate electronically excited states (denoted by horizontal lines with term and configuration) before reaching the ionization continuum (at 33,691 cm⁻¹ or 4.18 eV for Rb, and 45,932 cm⁻¹ or 5.69 eV for Sr).

**EXPERIMENTAL**

The LARIMS instrument used for this experiment comprises a vacuum chamber with a triaxial sample-positioning stage and a multi-bounce time-of-flight mass spectrometer, an ablation laser, strontium ionization lasers, rubidium ionization lasers, laser attenuators, laser power meters, a wavelength meter, a digitizer, timing control electronics, a computer, and software. We describe these components in the paragraphs below.

**Sample handling and positioning**

First, we photographed the stub of Zagami and GSD-1G under a binocular microscope, so that we could compare the sample before and after ablation, and so that we might compare and correlate the acquired Rb and Sr spectra with the photomicrograph after ablation. In this case, the sample was so fine grained that we were ultimately unable to recognize optical features that might correlate with variations in Rb and Sr content. Next we secured the stub with screws in a custom-designed jaw, and introduced the assembly into the vacuum chamber. There, we affixed the specimen jaw to the triaxial sample-positioning stage with a conical bayonet mount. The position of the stage is controlled by three piezo-electric drivers (Micronix PP-30 stages and PMC-100 controller) with closed loop positioning accuracy of ±10 nm over 30 mm of range.

The sample is driven into firm contact with the back of the sample electrode of the mass spectrometer (Fig. 3), then backed away by 200 μm to prevent deformation of the electrode (and hence of the electric field). This electrode has a 100 μm hole through which the ablation laser beam passes to reach the sample, and through which ablated atoms emerge to interact with the resonance laser beams. The depth of focus of the ablation laser optic is ±50 μm, and is mounted on a motorized stage (Micronix PP-8, 8 mm range, ±10 nm accuracy). We observe that adjusting the ablation focus particularly influences the measured abundance of strontium, presumably because strontium is less volatile than rubidium, so that it requires tighter focus to affect more efficient ablation. We therefore adjust the focus to
optimize strontium peak height before making hundreds of measurements; in general, the focus does not significantly change from run-to-run.

Initially, the sample is manually moved to ~10 locations estimated to bracket the location of the sample and the standard, and preliminary Rb and Sr LARIMS measurements are taken. The signals from the three materials (Zagami, standard, and epoxy) are generally easily distinguished. We use these data to bound the area for detailed measurements, which consist of spot analyses at hundreds of locations on a grid of points on Zagami and on the standard. Every spot analysis consists of 1800–2400 individual time-of-flight spectra, each from a single ablation pulse. The first spot analysis, and every 5th spot analysis thereafter, is taken on the standard; however, the locations on both the sample and the standard are measured in a random order, to separate and identify potential spatial and time-dependent instrument biases.

Sample ablation

At each analysis spot we ablate the surface using a Big Sky Centurion diode-pumped solid state Nd:YAG laser, frequency quintupled to 213 nm. This laser produces pulses of ~0.6 GW/cm². Approximately 1 μs after ablation, and after the ions created directly by ablation have been accelerated away from the remaining cloud of neutral atoms, we illuminate the cloud with our resonance lasers, first with the lasers tuned to rubidium transitions, and ~2 μs later with the lasers tuned to strontium transitions. The delay between Sr and Rb ionization separates the ion bunches in the mass spectrometer, allowing the independent measurement of the elements. The strontium laser system produces the radiation at 461 nm, 554 nm, and 1064 nm needed to resonantly excite and ionize Sr atoms (Fig. 2). The 1064 nm light is produced by a Quantel YG-980 Nd:YAG laser, and this laser also produces a frequency-doubled beam at 532 nm. The 532 nm beam is used to pump a Coherent ScanMate Pro dye laser with Fluorescein 548 dye from Exciton Inc., to produce 554 nm light. The 461 nm light is produced by a OPOTek Opolette 355 tunable optical parametric oscillator laser.

Similarly, the rubidium laser system produces the 780 nm, 776 nm, and 1064 nm light needed to resonantly excite and ionize Rb (Fig. 2). The 1064 nm light comes from a Continuum Powerlight 8020 Nd:YAG laser, whose frequency-doubled 532 nm radiation is used to pump a Continuum ND6000 dye laser with LDS-765 dye to produce 776 nm laser light. A second OPOTek Opolette 355 is used to produce the 780 nm laser light. The OPOTek lasers have bandwidths of ~0.6 nm, and the dye laser bandwidths are ~20 pm.

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Laser diagnostics

The ablation laser (213 nm), the lasers exciting the first resonance steps for Sr and Rb (461 nm and 780 nm, respectively), and the lasers exciting the second resonance steps (554 nm for Sr and 776 nm for Rb) are monitored with five GenTec EO M-LINK meters with QE-8 energy detector heads. These sample partial reflections from each beam, and record a signal proportional to the energy of every laser pulse. It is important that every laser produce pulses of consistent energy over hours, since changes can lead to unexpected fractionation of Rb from Sr. We have not yet implemented monitoring of the 1064 nm lasers; however, because the 1064 nm light is frequency doubled to pump the dye lasers, we would detect degradation in pulse energy by monitoring the output of the dye lasers.

We control the outputs of the lasers driving the first and second resonance steps (i.e., 461 nm, 554 nm, 776 nm, and 780 nm) using a pair of Thorlabs FW-102 filter wheels with absorptive neutral density filters with optical densities up to 4 for each beamline. Both 1064 nm beams are attenuated using a Newport 935-10 high power attenuator. Typical laser pulse energies and beam diameters are listed in Table 1.

We monitor the wavelengths of the tunable resonance lasers (i.e., 461 nm, 554 nm, 776 nm, and 780 nm) using a Toptica WS-6 wavemeter with a multichannel opto-mechanical switch that sequentially measures the wavelength of each beam, cycling through four lasers several times each minute. We routinely observe stability of <1 cm$^{-2}$ over entire runs, lasting hours to days.

Multi-bounce time-of-flight mass spectrometer

Our time-of-flight mass spectrometer (Fig. 3) consists of an ion source, flight tube, two reflectors on opposite ends of the flight tube, and a detector, all aligned coaxially. The ion source is located between two electrodes: the sample electrode, with a 100 μm aperture for the ablation laser light to pass through, and for the ablated atoms to emerge from; and the extractor electrode, with a larger aperture through which ions are steered toward the flight tube. The sample electrode is pulsed from -1500 V, when we are retarding the electrons, their separation increases and the temporal width of the bunches decreases, allowing us to clearly delineate the peaks for $^{84,86,87}$Sr and $^{85,87}$Rb. Because we use a ~2 μs delay between Sr and Rb resonance ionization to separate the elements, the greatest demand for mass resolution that we place on the spectrometer is the ability to resolve isotopes 1 u apart; thus, the mass spectrometer can operate in a low-resolution mode with only five bounces, achieving a mass resolution of $m/\Delta m \approx 200$. After five bounces, the second reflectron is de-energized, we lower the electrode voltage that has protected the ETP MagneTOF hybrid discrete dynode detector from unwanted ions produced directly by ablation, and the resonance ions are allowed to reach the detector. The resulting pulses are directly digitized using a Gage Razor 16-bit digitizer, sampling every 5 ns, with a bandwidth of 125 MHz.

Timing, computer, and software

The entire sequence of ablation, resonant photoionization, multi-bounce flight of the photoions through the mass spectrometer, and detection is repeated at 20 Hz. A typical spot analysis includes 1800–2400 repetitions, and an equal number of backgrounds in which some or all of the resonance lasers are not fired. The timing and synchronization of all the components of the instrument are regulated using Highland Technologies T560-4 digital delay generators. The entire instrument is controlled by a desktop computer running custom LabVIEW (National Instruments) software.

Data analysis

The data that we present here include 711 spot analyses on Zagami and 182 spot analyses on the GSD-1G standard. These analyses were acquired in four separate measurement series.

Table 1. Typical laser parameters for this experiment. Because of the lower pulse energies available to drive the 780 nm and 776 nm transitions in Rb, these beams were focused to a smaller diameter. Beam diameters are approximate because the beam profiles were irregularly shaped. Typical pulse durations were ~5 ns for the ablation laser and 10–15 ns for the resonance lasers.

| Laser Source                  | Wavelength (nm) | Pulse energy (μJ) | Beam diameter (mm) |
|-------------------------------|-----------------|-------------------|--------------------|
| **Ablation**                  |                 |                   |                    |
| Big Sky Centurion Nd:YAG, 5th harmonic | 213             | 225               | 0.1                |
| Sr resonance ionization       |                 |                   |                    |
| OPOTek Opolette 355           | 461             | 1350              | 4                  |
| Coherent ScanMate Pro, Fluorescein 548 dye | 554             | 65                | 4                  |
| Quantel YG-980 Nd:YAG         | 1064            | 2120              | 10                 |
| **Rb resonance ionization**   |                 |                   |                    |
| OPOTek Opolette 355           | 780             | 3                 | 0.5                |
| Continuum ND6000, LDS-765 dye | 776             | 2.5               | 0.5                |
| Continuum Powerlight 8020 Nd:YAG | 1064           | 2140              | 10                 |
runs, each including Zagami and GSD-1G spots (with the latter at intervals of every four Zagami spots) from March to June 2014.

Each spot analysis consisted of an interval of sample conditioning by the ablation laser, typically lasting for ~10,000 pulses, followed by a background-and-data acquisition sequence. The background-and-data acquisition typically lasted 3600–4800 ablation pulses in repeated groups of 200. During the first 40 pulses in each group, the optical parametric oscillators that excite the first resonance transition for each element were fired, but the dye lasers and Nd:YAG lasers that then ionized the excited atoms were not. During each of the next 40 pulses, the dye lasers and the Nd:YAG lasers were fired, but the first-step resonance lasers were not. The signals recorded from these pulses allowed us to assess backgrounds due to photoionization by our resonance lasers of species other than Rb and Sr (Fig. 1). These pulses were followed by 20 pulses without any resonance lasers firing at all; these were to determine our backgrounds due to ionization by the ablation process itself, as well as detector and digitizer noise. These pulses were followed by 100 ablation pulses that were each accompanied by the full complement of resonance lasers, in which we obtained our Rb and Sr signals.

The detector voltage for each pulse was recorded and digitized at 5 ns intervals from 95 μs to 100 μs after ablation. Since the zero level on our detector fluctuated on the ~1 s timescale, we corrected the signal from each pulse by subtracting the most common value, which we adopted as a timescale, we corrected the signal from each pulse by subtracting the mean value, which we adopted as an estimate of the baseline voltage.

The data that we report here were all acquired with relatively high ablation laser intensity. Like others (e.g.,[65]), we have struggled to obtain high reproducibility from the laser ablation process. However, work by Poitrasson et al. [66] and Liu et al. [67] showed that femtosecond laser ablation produces ejecta that is more nearly stoichiometric and reproducible than nanosecond lasers such as we have been using. Russo et al. [68] reviewed some of the advantages of femtosecond ablation for precise analysis. Specifically, reproducibility increases with ablation laser intensity, and R.E. Russo (personal communication, 2014) suggested that we might obtain some of the benefit of femtosecond ablation if we could achieve an ablation intensity greater than ~1 GW/cm². In the present work we approached this criterion as best we could with our existing ablation laser, which produces up to ~225 μJ of 213 nm light in ~5 ns pulses. Focused to a ~100 μm spot, this corresponds to approximately 0.6 GW/cm²; however, our uncertainty in this value is considerable, since we monitor intensity only indirectly during data acquisition, using a partial reflection from the ablation laser beam. We are planning a future suite of experiments with a femtosecond ablation laser.

The time-of-flight spectra that we obtain under these conditions are qualitatively different from what we formerly observed (e.g.,[69]), when we had been attenuating ~90% or more of the ablation laser beam. The most important difference is that, during the sample conditioning period, the Sr isotope peaks are absent from our time-of-flight spectra, replaced by a low, broad smear. Rb peaks disappeared similarly when we tried to photoionize Rb 1 μs after ablation, rather than at its typical delay of >3 μs. We attribute this effect to the development of a plasma of ablated material in front of the sample. The plasma shields the photoions from the extraction field of the mass spectrometer’s ion optics, leading to smearing of the isotopic peaks. Although the plasma appears to have been present when we tried to photoionize Sr, ~1 μs after ablation, it had dispersed by ~3 μs after ablation.

Over a few thousand ablation pulses, the longevity of the plasma decreased, and we could eventually photoionize Sr at ~1 μs after ablation without interference from the plasma. Unfortunately, we could not avoid waiting for the plasma to dissipate more quickly by delaying the photoionization of Sr by more than about 1.1 μs, since Sr atoms are evidently ablated from the sample with high speed, and they would quickly pass through the laser interaction region. Even after waiting for several thousand pulses, occasional pulses still show the effects of the plasma. These pulses were easily identified by their high, broad signals ~300 ns after the usual arrival time of the 86Sr peak (corresponding to a mass of 88.6 u), and by their concomitantly low 88Sr signal. To avoid biases from these data, we excluded spectra with 88.6 u signals that were >4σ above the mean background (removed data constituted <2% of all spectra).

We integrated peaks for each of the isotopes 86,87,88Sr and 85,87Rb from the time-of-flight spectrum for each pulse, after defining time intervals of interest for each isotope based on the spectra of the GSD-1G standard. We evaluated the mean signal for each isotope by computing the mean of its integrated peak from the pulses with all the resonance lasers firing, and correcting for the mean integrated peak in each type of background pulse (the background integrals taken with some of the resonance lasers firing were themselves first corrected for the background integrals that assessed the direct ionization from ablation). We assessed our statistical confidence in these mean signals by computing the standard error, summing the variances among the integrals measured in each type of pulse. Although the integrals from individual pulses are distributed in a strongly non-Gaussian way, the standard error of the mean is still a valid estimate of confidence, as we could assemble many populations of integrals at random from their actual distribution, and find that the means of each population cluster around the mean of the actual population of integrals with a spread given by the standard error.

Isotope integrals vary greatly from one spot on Zagami to another, which is to be expected since the meteorite, although fine-grained, is mineralogically and chemically heterogeneous. We excluded from our subsequent analysis any spot at which the detection of one or more of the isotopes 86,87,88Sr and 85,87Rb was weaker than the 95% confidence level. This removes data with high uncertainty that would poorly constrain the age of the specimen. We stress that this is the only criterion that we employ for excluding spots of Zagami from our analysis; we are not otherwise picking the ‘best’ or ‘cleanest’ signals in any way. In the present experiment, this low-signal exclusion criterion removes 130 spot analyses out of 711 attempted, leaving us with 581 data points with robust detection of both Rb and Sr.

The integrals of the five isotopes exhibit significant covariances. These have a physical origin in the inevitable pulse-to-pulse fluctuations in the intensity of the ablation laser, which are ~3–5% in our system. Because of the strong nonlinearity of laser ablation, even these modest fluctuations in intensity produce fluctuations of ~100% in signal.
Likewise, integrals of isotopes of the same element also fluctuate together because of fluctuations in their respective resonance lasers. We calculated and accounted for all the covariances when we computed isotope ratios.

We used the analyses of GSD-1G reference glass to determine the instrumental fractionation among the isotopes as a function of time during each run. Figure 4 shows that the fractionation between isotopes of the same element is typically modest, but that the elemental fractionation between Rb and Sr is considerable, and often variable. On some days we observe the elemental fractionation to vary only slightly, whereas, on other days, we see large changes as a function of time (Fig. 4). Ultimately, we do not know the causes of these changes, although we have seen some correlations between greater overdetection of Rb relative to Sr and cooler laboratory temperatures. Our earlier measurements were affected by fluctuating temperatures overnight, when the laboratory air conditioning was turned off, and during the summer, when the laboratory temperature exceeded 30°C. Since that time, we have taken great pains to ensure a nearly constant temperature in our laboratory, including the installation of a high-capacity air-handling system that runs continually, and circulating chilled water to stabilize the temperature of laser dyes and the OPO laser heads. We presently observe residual temperature fluctuations of ~0.5°C in the laboratory. While we continue to search for root causes of the fluctuations in instrumental fractionation, for the moment we are limited to monitoring them and correcting for them. We estimate the fractionation of each isotope relative to $^{86}\text{Sr}$ at the time that each Zagami analysis was performed by interpolating between the calculated fractionations at the time that GSD-1G was analyzed.

After correcting each isotopic signal for the instrumental fractionation, we compare $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{87}\text{Rb}/^{86}\text{Sr}$ ratios from the Zagami spot analyses. The isochron diagrams shown in Fig. 5 show this comparison, and we discuss their significance in the next section.

**RESULTS**

We analyzed the Zagami meteorite (and the GSD-1G standard) with ablation intensity of ~0.6 GW/cm² on four separate occasions in early 2014. These four runs differed in certain respects, as we continued to modify and upgrade our instrument during this period. For example, during the run beginning on 7 March, the ablation beam was passed through an attenuator that we had previously used, although the attenuator was set for maximum transmission. For the 12 March run, we removed the attenuator completely from the beam path, eliminating a few optical interfaces, and therefore transmitting an ablation beam that was ~25% brighter. Before the 15 May run, we replaced our aging detector with a new unit of the same model, and before the 28 May run we strengthened the rejection scheme in our time-of-flight mass spectrometer for ions produced directly by ablation by pulsing the voltage on the electrode in front of the detector. Because data from these four runs were not acquired under identical conditions, it may be best to evaluate their results separately. On the other hand, since each run included analyses of the GSD-1G standard, it also seems reasonable to combine the standard-corrected data from all the runs into a single analysis. We therefore present both separate and combined analyses.

The four runs include two very long runs and two that were aborted after a relatively small number of spots were analyzed. Specifically, for the 7 March run we analyzed 85 spots on Zagami (and 22 spots of GSD-1G) before the water-cooling system for one of the rubidium resonance lasers failed, 18 h into the run. Next, we completed a 52 h run beginning on 12 March, in which we analyzed 250 spots on Zagami and 64 spots on GSD-1G. This was followed by a run beginning on 15 May during which we analyzed 56 spots on Zagami (and 15 on GSD-1G) before aborting after 20 h out of fear for the integrity of the new detector that we had just installed. Finally, the 28 May run analyzed 320 spots on Zagami and 81 on GSD-1G over nearly 120 h of continuous

![Figure 4](image-url)
operation. The two aborted runs highlight failure modes for our experiment that we are working to eliminate, and, because of the runs’ smaller number of spot analyses, they have poorer precision than we have otherwise obtained. The duration required for a run is presently controlled by our need to spend ~85% of our ablation pulses conditioning the sample and out-waiting the plasma, and only ~15% of the time was spent collecting resonance data and backgrounds. Our hope is that ultimately replacing our ablation laser with a femtosecond laser, or even a nanosecond laser with a higher repetition rate, will allow us to relax the requirement of such lengthy conditioning times.

Figure 5 shows the isochron diagrams for each of the four runs. The ages are calculated from the slopes of the best fitting lines using the value of the $^{87}\text{Rb}$ half-life determined by Rotenberg et al. Our only criterion used to reject a spot analysis from an isochron is failure to unambiguously detect one or more isotopes.

![Figure 5. Zagami isochron diagrams for the four data runs described in the text. Dots represent individual spot analyses, with ellipses denoting their respective 1σ uncertainty intervals. The best-fitting line for the data from each run is shown, along with its 1σ uncertainty interval (dashed). The age is calculated from the slope of the best-fitting line, using the $^{87}\text{Rb}$ half-life determined by Rotenberg et al. The only criterion used to reject a spot analysis from an isochron is failure to unambiguously detect one or more isotopes.](image)
more on the abundances of Rb and Sr in our analyses than on the age of the specimen. For the Boulder Creek Granite, Peterman et al.\textsuperscript{[70]} observed 10–426 ppm Rb and 17–661 ppm Sr, which is considerably more of both elements than in Zagami (1–60 ppm Rb, 4–210 ppm Sr\textsuperscript{[44]}).

All four isochron ages agree broadly with the more precise ages determined for Zagami by Shih et al.\textsuperscript{[46]} Nyquist et al.\textsuperscript{[45]} and Borg et al.\textsuperscript{[44]} who obtained uncertainties as small as a few million years using thermal ionization mass spectrometry. The disparity between the precision obtained in these experiments and the precision that we achieve of several hundreds of millions of years arises from two differences between our respective techniques. First, unlike in a typical thermal ionization mass spectrometry experiment, we did not make any effort to select pristine mineral separates or spots for analysis. On the contrary, the ensemble of spots that we analyzed was simply a rectangular grid of points on the polished surface of the meteorite specimen. Therefore, many of the spots that we analyzed could have been slightly altered by grain-grain interactions or grain-fluid interactions in ways that would have altered their abundances of Rb or Sr. An effort to date the meteorite with the highest achievable precision would tend to exclude such mineral grains after thorough inspection and characterization, but we have avoided these steps to mimic the operation of an instrument like ours in a spaceflight context, where such careful spot selection is probably impractical.

Second, whereas isochrons obtained with thermal ionization mass spectrometry have a relatively small number of individual analyses, each performed with high precision, our isochron consists of a very large number of lower-precision spot analyses (limited ultimately by the number of atoms that we ablate, resonantly ionize, and detect). The precision of our age determinations comes from the statistics of our analyses, which in our case is constrained by comparatively few analyses with relatively high Rb/Sr ratios. For instance, the \(\sim 1\%\) of the spots that we analyzed that yielded Rb/Sr ratios >10 have large uncertainties, but they also exert a great deal of leverage on the slopes of the isochron lines. Our precision on the ages would be improved if we were to systematically search for more spots in the specimen with high Rb/Sr ratios that would further constrain the slopes of the isochron lines.

However, one might rightly worry that favoring the analysis of spots with unusually high Rb/Sr ratios, which by virtue of their rarity must represent materials that do not comprise the bulk of the specimen, might give a distorted view of how well the Rb and Sr have been fixed in the mineral phases since the formation of the specimen, and therefore of its age. For the sake of comparison, all the Zagami analyses of Borg et al.\textsuperscript{[44]} had Rb/Sr ratios <2; it is conceivable that the spots that we analyzed with much higher Rb/Sr ratios might represent trace secondary phases. If so, it is remarkable that these spots nevertheless yield Rb and Sr isotopes in proportions consistent with the \(\sim 160–180\) Ma ages reported by Shih et al.\textsuperscript{[46]} Nyquist et al.\textsuperscript{[45]} and Borg et al.\textsuperscript{[44]} Future analyses of other samples will tell whether we continue to obtain reliable ages from spot analyses in raster patterns, as we perform now, or whether we need to pre-select analysis spots by restricting our attention to pristine-looking mineral grains, for example.

The values determined for initial \(^{87}\text{Sr}/^{86}\text{Sr}\) ratios are 0.736 ± 0.006 and 0.730 ± 0.001 in the two runs from March, and 0.719 ± 0.002 and 0.720 ± 0.001 in the more recent runs. The latter pair of values are consistent with the non-radiogenic \(^{87}\text{Sr}/^{86}\text{Sr}\) ratio of 0.72157 ± 0.00008 determined by Borg et al.\textsuperscript{[44]} and therefore with the inference that Zagami is one of the most evolved meteorites yet found from Mars. However, our values from the earlier runs differ from this value by more than 2\(\sigma\). We do not yet understand how or whether the instrumental changes that we made between March and May 2014 (chiefly the installation of a new detector, but we also re-polished the sample surface and made a number of small changes to the resonance lasers) caused the improvement in our ability to correctly determine

![Figure 6](image-url)  
**Figure 6.** Zagami isochron diagram with data from all four runs with bright ablation laser pulses. Symbols are as in Fig. 5. Although the four runs were performed with slightly different experimental conditions, it may be appropriate to combine their data in this way, because the data from each run was standardized using GSD-1G analyses. The right panel shows the same data as the left panel, but with a logarithmic scale on the horizontal axis so that the large number of points with low Rb/Sr ratios are better resolved.
the \(^{87}\text{Sr}/^{86}\text{Sr}\) ratio of the non-radiogenic component. Nevertheless, we are looking closely at this question in our ongoing measurements.

The mean square weighted deviation (MSWD; i.e., \(\chi^2\) per degree of freedom) between our data and the best-fit line through them is between 1.4 and 1.9 for all four runs. This compares quite favorably with the MSWD of 17 quoted by Borg et al.\(^{44}\) for their “representative” isochron, but at least part of that discrepancy arises from our larger uncertainties on the individual analyses. However, in an absolute sense, our MSWD values are quite large: the most statistically favorable case is the 15 May run, in which we obtained an MSWD of 1.9 from 35 points. A mean square residual this large from a truly linear data set of this size occurs in random trials only \(<0.1\%\) of the time. The probability that our data can be explained as a statistical line subject to random jitters of a size given by our uncertainty is even smaller for the other runs: a 238 point line (as in the 12 March run) yields an MSWD of 1.4 or greater only \(<0.002\%\) of the time, and the probabilities of random errors having given rise to the MSWD values that we obtained on 7 March and 28 May are \(<0.001\%\). These considerations imply that either (a) our estimated uncertainties under-report the actual random errors by as much as a factor of \(~1.4\), or (b) the \(^{87}\text{Sr}\) in Zagami is not a strictly binary mixture of radiogenic Sr from an isochronous event affecting the entire specimen and an isotopically homogeneous non-radiogenic component. Quite possibly both these explanations are true, to at least some extent. The large MSWD in the “representative” isochron of Borg et al.\(^{44}\) certainly suggests that, in detail, the \(^{87}\text{Sr}\) in Zagami deviates from a strictly isochronous binary mixture.

A synthesized isochron diagram showing all 581 spot analyses from our four runs together is shown in Fig. 6, both in linear space, where the isochron is a straight line, and in logarithmic space, where the many analyses with relatively low Rb/Sr ratios are more easily seen. The inferred age, \(360 \pm 90\) Ma, is higher than the \(~180\) Ma age determined by Shih et al.\(^{46}\), Nyquist et al.\(^{45}\) and Borg et al.\(^{44}\), however, our age is consistent with theirs at the 2\(r\) level. Likewise, the error-weighted average age from our four runs is also consistent with these, at \(270 \pm 90\) Ma.

CONCLUSIONS

Our analyses of the Zagami meteorite represent the first successful application of resonance ionization mass spectrometry to isochron geochronology. Operating with ablation laser intensity of \(~0.6\) GW/cm\(^2\), we obtained \(^{87}\text{Rb}/^{86}\text{Sr}\) isochron ages consistent with the \(~180\) Ma age of Zagami determined by thermal ionization mass spectrometry in all four runs that we attempted. In the two runs that were completed, we achieved precision of \(200\) Ma or better, meeting the criterion that NASA has established for \textit{in situ} dating.\(^{121}\)

One of the key reasons that the intense ablation pulses were necessary was to minimize elemental fractionation during the laser ablation process. Fractionation prior to photoionization is an atypical concern for a resonance ionization mass spectrometry experiment; one of the advantages of this technique for many applications is that, since atoms are ionized from the vapor phase rather than directly from a solid sample, there is no matrix-induced isotopic fractionation that differs between a sample and a standard. There are, of course, isotope shifts and odd-even effects that lead to spectroscopic fractionations, but these generally affect samples and standards to the same extent. In our work, because we need to analyze two elements, we found ourselves once more subject to often irregular and unpredictable fractionation between the two elements, even when comparing replicate analyses of standards. Operating the ablation laser at high intensity has allowed us to obtain accurate and reproducible results.

Among the most important contributions that a resonance ionization mass spectrometer can make to the already formidable arsenal of geochronological techniques is that, as we have noted, it is readily miniaturizable for spaceflight and \textit{in situ} dating on other planetary bodies. Towards this goal, we have designed two successively smaller versions of our instrument to work with core or rock samples. The first of these is itself a working instrument with dimensions of \(40 \times 50 \times 180\) cm\(^3\); we have already used it (without resonance lasers) to analyze organic molecules in a chip of the Murchison meteorite.\(^{71}\) We are presently implementing the miniaturized resonance lasers that accompany this instrument; the laser systems for each element have volumes of only \(~1500\) cm\(^3\), a reduction in size from our current resonance lasers of a factor of \(>100\).

The second, even smaller instrument still exists only as an engineering design, but it will have a mass of \((14.5\) kg, energy demand of \(<650\) W/h for a complete run, and a volume of \(~16,000\) cm\(^3\) \((~25\) cm on each side) including the mass spectrometer.\(^{72}\) The design takes advantage of several components that have already been developed for spaceflight, including the time-of-flight mass spectrometer (currently under construction for flight to the Moon on Luna-Resurs, and built by the University of Bern\(^{73–75}\)), vacuum system (developed by Creare), electronics (developed at Southwest Research Institute), and the sample-handling system (designed by MacDonald, Dettwiler and Associates). The ablation and resonance lasers will be fiber laser systems built by Aerospace Corporation, which are advantageous for their exceptionally small volume and for the fact that they have relatively few optical interfaces that could become contaminated by outgassing of other components while in space. By using the lasers in different combinations, the instrument will also be capable of performing laser ablation mass spectrometry to produce maps of organic molecules, both at microscopic scales crucial for establishing geologic context.

While our successful dating of Zagami shows that our instrument is capable of dating a single planetary specimen, we are of course aware that Solar System history is recorded in rocks of diverse chemistry, mineralogy, and petrology. We are beginning experiments to test and refine our instrument and technique by dating a suite of rocks of increasing analytical difficulty. For example, the Boulder Creek Granite is richer in Rb and Sr than Zagami, but appears to have recorded one or two post-crystallization events in certain mineral phases.\(^{20}\) To be able to recognize this behavior, we are working on means of mineral identification from our data for each spot analysis. To date a second sample in our collection, the lunar meteorite NWA 032, we must be able to improve our precision in spite of the scarcity of Rb \((1–5\) ppm\(^{25}\)) in this sample and in lunar materials in general. As an analogue for
Martian rocks that have experienced significant hydrothermal alteration and partial resetting of radiogenic systems long after formation, we will examine the Fountain Formation sandstone, which was deposited at ∼290 Ma and which has experienced K-metasomatism at ∼135 Ma and ∼94 Ma.[77,78] Distinguishing primary and secondary ages in the isotopic data will be important for the future study of Martian rocks with suggestions of hydrothermal alteration, such as cemented hematite, sulfates, chlorides, and phyllosilicates. Finally, to assess our ability to investigate one of the oldest samples in the Solar System (age of 4.6 Ga), we will examine the eucrite Juvinas, which poses an additional analytical challenge because of its very small range of 87Sr/86Sr.[79] The challenges of acquiring and interpreting geochronological data from this suite of rocks exemplify the analytical challenges inherent in dating samples in situ elsewhere in the Solar System.

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