AN IN-SITU RB-SR DATING & LIFE DETECTION INSTRUMENT FOR A MER+ SIZED ROVER: A MSR PRECURSOR. F.S. Anderson<sup>1</sup>, J.H. Waite<sup>1</sup>, J. Pierce<sup>2</sup>, K. Zacny<sup>3</sup>, G. Miller<sup>1</sup>, T. Whitaker<sup>1</sup>, K. Nowicki<sup>1</sup>, P. Wilson<sup>1</sup>, <sup>1</sup>Southwest Research Institute, Boulder, CO 80302 (anderson@boulder.swri.edu), <sup>2</sup>JP Innovations, Monroe, WA 98272, <sup>3</sup>Honeybee Robotics, Pasadena, CA 91101.

Introduction: We posit that a Mars in-situ life detection and geochronology mission that will triage and validate samples for Mars Sample Return (MSR) is technically feasible in the 2018-2022 time frame. During the 2008 Decadal Survey community outreach effort, the required technology for such a mission had not yet been demonstrated, and hence the planned caching rover instrument suite could not directly address life detection and dating, the core science issues of MSR. However, today these technologies are moving from lab prototypes to field deployable instruments, and provide an opportunity to directly address the science goals of MSR within the bounds posed by current scientific, fiscal, and political pressures on the Mars program.

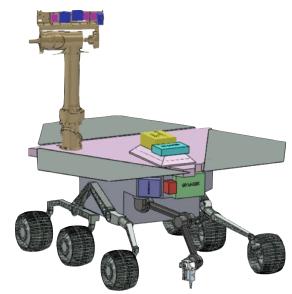
**Architecture Bounds:** We believe that new technological advances enable a mission concept that addresses the competing scientific, political, and fiscal requirements for flight in this decade. Specifically, the mission must:

- 1) be responsive to the astrobiological and chronological science goals of the MEPAG [1], Decadal Survey (DS) [2], and E2E-iSAG [3];
- 2) address the physical/chemical/biochemical surface materials "Strategic Knowledge Gaps" (SKGs) for human exploration of Mars [4];
- 3) avoid the MSR *appearance* of long term political commitment and cost.

These requirements can be accomplished by a minimum of a lander, but more optimally by a rover.

**Mission Concept:** As a precursor to MSR, we propose a Mars Exploration Rover (MER) to mid-sized rover to carry out life detection, organic characterization, geochronology, and mineralogy measurements (**Fig. 1, Table 1**). The rover requires an arm and drill with coring and abrading bits [5-7]. JPL has reassessed the MER entry, descent and landing system performance with the data acquired from the MER landings, and determined that the system is capable significantly higher landed mass (~40-60 kg before reserve) and somewhat larger instrument volume (~80,000 cm<sup>3</sup>) [8]. The larger science payload allows for more sophisticated instruments, including those required for in-situ dating and life detection.

The instruments are an integrated package sharing a high-resolution zig-zag time of flight mass spectrometer (ZZ-TOF) and a small trochoidal mass spectrometer (TMS [9-11]), capable of extensive analysis of biotic and abiotic chemistry, which when combined with a laser desorption resonance ionization ion source



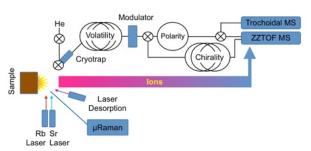
**Figure 1:** Redesigned MER sized rover with IDD arm, Honeybee coring drill, and proposed mission payload (pers. comm. C. Kahn, B, Jordan, JPL, 2012; pers. comm. K Zacny, 2012).

Table 1: Concept details

Payload Component	TRL	Cost (M\$)	Mass (kg)	Power (W)	Total Power (W-hrs)/ Date	Total Power (W-hrs)/ Bioassay	Volume (cm³)
Shared ZZTOF & Electronics	5	22	10.0	5	43.8	3	12000
3 Pumps	9	2	1	3	25.0	48	92
Sample Handling	3	3	2	1	-	1	640
XYZ stages	4	1	0.3	-	-	-	1033
XYZ Controller	4	1	0.5	5	0.4	-	1080
ADC	5	4	1	4	50	2	36
Astrobiology Source	4	2	0.3	0.5	-	0.25	7
Cryotrap (Rycor)	6	2	2.5	6	-	36	190
GCxGC	4	4	2.5	5	-	30	70
Cycloid	5	10	2.0	1.5	-	9	3000
Dating Source	-	4	0.3	0.5	6.25	-	-
Ablation Laser	5	3	1	3	38	-	306
Sr Laser	4	4	2.5	6	75	-	1418
Rb Laser	4	3	2.1	5	63	-	1170
Fiber harnesses	-	-	0.5	-	-	-	-
uRaman & electronics	5	8	2.3	5	4	-	2400
Probe	5		0.2	-	-	-	299
Spectrograph	5		-	-	-	-	950
Arm (IDD)	9	10	2.5	-	-	-	-
Drill/Coring/Abrading/scoop	5		1.5	45	8	8	168
Cameras x3	9	5	0.795	2	12	12	94
Camera electronics x3	9						472
Totals		88	35.7		324	148	24952

can sensitively measure isobar free Rb-Sr isotopes for geochronology (**Fig. 2**). The desorption laser is also used with a μRaman/LIBS for mineral characterization, which in combination with the ZZ-TOF, will additionally provide measurements of K-Ar isotopes for a second form of radiometric dating [12].

Life Detection & Organic Characterization: Consensus is rapidly growing that definitive extra-



**Figure 2:** Instrument concept. Samples are desorbed by a 213 nm laser and either cryotrapped for transfer to the organic analysis and life detection subsystem, or illuminated by the resonance ionization lasers for Rb-Sr analysis. The desorption laser also produces 532 nm light used by the  $\mu$ Raman/LIBS to identify secondary minerals in the desorption spot. Finally, LIBS will be used to measure K, and the ZZ-TOF Ar, providing a second chronometry measurement.

terrestrial life detection and organic characterization requires "gold-standard" triple coincidence correlation techniques using compound pattern recognition, isotopic fractionation, and determination of chirality of organic molecules [13]. Specifically:

- a) Organic pattern recognition: In general, abiotic organic homologous compounds exhibit a decreasing abundance with increasing chain length; deviations from such a distribution is a signpost of pre-biotic chemistry [14].
- b) Isotopic fractionation: The majority of autotrophic metabolisms on Earth discriminate against the heavy isotopes (C,N) by photolytically driven fractionation, including from the results of photosynthesis, nitrification, denitrification, sulfate reduction, sulfide oxidation, methane oxidation and methanogenesis [15, 16].
- c) Chirality: A preponderance of biologically formed compounds are synthesized exclusively of identical enantiomers, which are believed to be a universal signature of living systems [17].

Hence, determining organic patterns, compoundspecific C and N isotopic ratios, and chirality of each compound within the chemical pattern is the most generally applicable and conclusive way to identify extant or fossil life.

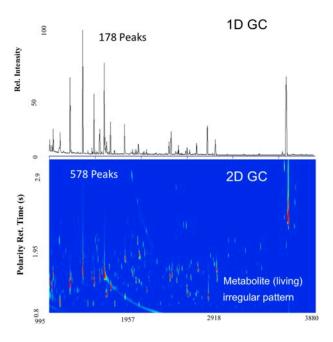
One-Dimensional Gas Chromatography: Current in-situ technology for interpretation of organic signatures on Mars have focused on one-dimensional gas chromatography (1D-GC) mass spectrometry [18, 19]. The GC subsystem ingests gases produced from heated samples, and separates evolved organic compounds (Fig. 3a). However, single GC separations (1D-GC) typically only achieve partial separation composed of

	Quad GS- MS	2D-GC- TOF-MS
Sensitivity	ppb	ppt
Total peaks in 30 min.	~80	~5500
Spectral skewing	Yes	No
Pattern recognition	No	Yes

Table 2: 1D-GC versus 2D-GC

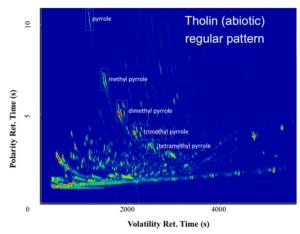
5-10 intermixed compounds, totaling ~80 intermixed peaks in 30 minutes, complicating interpretation (called spectral skewing) and eliminating the possibility of pattern recognition; finally, 1D-GC systems typically have part-per-billion sensitivity (**Table 2**). As a result of these limitations, 1D-GC systems focus on issues of habitability, not astrobiology.

Two-Dimensional Gas Chromatography: We are developing 2D-GC instrument capable of concentrating compounds in a cryotrap and then emitting them into a 2D-GC, enabling the separation of all compounds and compound pattern recognition (Fig. 3b, 4; Table 2). The output of the first volatility GC is concentrated by a modulator for a brief time (increasing the sensitivity by ~1000X), and then burst to the polar-

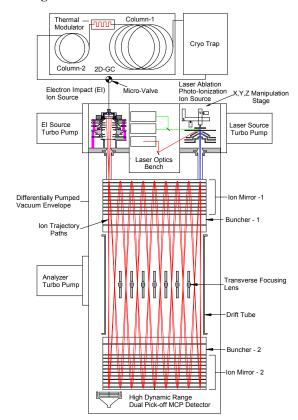


**Figure 3: a.** Example of 1D-GC output. Each peak is composed of multiple intermixed compounds. **b.** Example of 2D-GC of the same compound. Note single peaks in **a** are now separated into multiple peaks in the second dimension. The irregular pattern of compounds is indicate this sample contains metabolites, and is from a living organism.

ity or the chirality GC. The polarity elutant is split between the ZZ-TOF and a TMS for isotope measurement. This system enables the user to assess the overall pattern of compounds, as well obtain a mass spectrom, chirality, and isotopes for each compound, without intermixing.



**Figure 4:** 2D-GC illustrating irregular pattern associated with abiotic organic signature; compare with **Fig. 3b**.

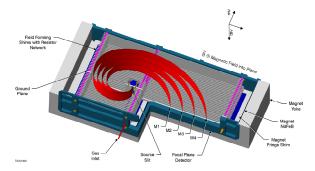


**Figure 5:** Zig-zag time of flight maintains high mass resolution and is much smaller than traditional TOF instruments.

The ZZ-TOF (**Fig. 5**) is an outgrowth of multibounce time of flight (MBTOF) technology that reduces the size of the mass spectrometer while maintaining the path length, ion focus [20, 21], and high heritage of MBTOF designs.

We determine all of the light isotopic ratios for C, H, N, O, P, S on individual compounds through split-flow of the effluent to a TMS (Fig. 6), with accuracy sufficient to identify biological isotopic fractionation (Fig. 7). This level of analysis is identical to that which would be performed in a terrestrial lab on a returned sample.

Geochronology: In-situ geochronology measurements better than ±200 Ma, and preferably using more than one isotope system, have long been a key goal for planetary science [22]. We have developed a relatively rapid, portable Rubidium-Strontium (Rb-Sr) dating technique based on laser desorption resonance ionization mass spectrometry (LDRIMS) for use on Mars and the Moon. We plan to demonstrate the instrument



**Figure 6:** TRL Design. Cut-away view of the operating principles of CFMS. Ion trajectories are shown in red. Magnetic field produced by a dipole magnet configuration is normal to the ion trajectories. A positive and negative plate produces the electric field and mass dispersion is linear on the focal plane for this arrangement.

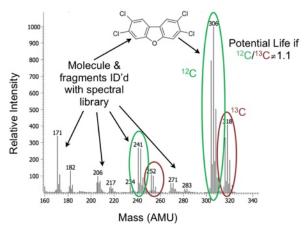


Figure 7: Isotopic indicators of life.

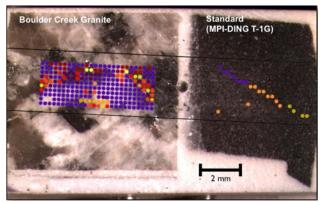
on meteorites such as Zagami (Mars) and NWA 032 (Lunar); however, before working with high value samples, we are validating the technique on terrestrial materials such as the Boulder Creek Granite (BCG). Using LDRIMS, we have succeeded at producing a moderate precision date for BCG of 1.72±0.087 Ga (n=288, MSWD=1). We ultimately expect to use ~1000 spot measurements (versus the 288 currently **Figure 8**), which combined with other instrument improvements should result in a precision of ~± 50 Ma [23]. We have succeeded at producing moderate precision dates of ±130 Ma (MSWD=1; **Fig. 9**); near term improvements should result in a final precision of ~±50 Ma.

Geochronology Implementation: The LDRIMS technique avoids the interference and mass resolution issues associated with geochronology measurements, and has miniaturization potential [23]. A sample is placed in the ZZ-TOF mass spectrometer and surface atoms, molecules, and ions are desorbed with a 213 nm laser. Ions are suppressed by an electric field and the plume of expanding particles is present for many μs, during which it is first illuminated with laser light tuned to ionize only Sr, and then 1-3 μs later, for Rb (Fig. 10) [24]. We have partially miniaturized the instrument (Fig. 11-12), including Sr lasers, ablation laser, and mass spectrometer, and will soon to start using the instrument for field measurements.

Our current prototype can measure the isotope ratio of lab standards with 10 ppm net Sr or Rb to a precision of  $\pm 0.1\%$  (1 $\sigma$ ), with a sensitivity of  $1:10^{10}$  in  $\sim 15$  minutes. The speed of the LDRIMS measurement allows thousands of samples to be measured in significantly shorter periods of time than traditional methods; sample preparation consists of rough cutting the sample to fit in our sample holder.

Currently we avoid biased secondary mineralogies using  $\mu$ FTIR of the samples (**Fig. 13**); in a flight configuration we will use a  $\mu$ Raman spectrometer that shares the LDRIMS ablation laser, and in combination with the ZZ-TOF, will enable simultaneous K-Ar measurement [12]. **Simultaneous Rb-Sr and K-Ar dates will significantly improve confidence to the ultimate scientific interpretation.** 

Addressing Requirements: The proposed instrument payload addresses req. 1 goals such as assessment "of the past and present habitability of Mars, whether life is or was present on Mars in its geochemical context, and characterize carbon cycling and prebiotic chemistry", as well as, "Determine the nature and evolution of the geologic processes…and characterize the … composition… and evolution of Mars's interior"



**Figure 8:** Locations and minerals used for LDRIMS measurement.

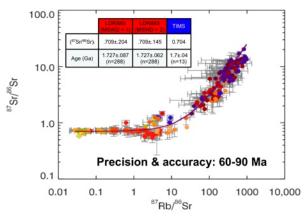
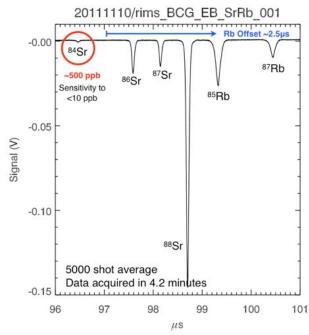


Figure 9: Calibrated repeat isochron of the BCG.



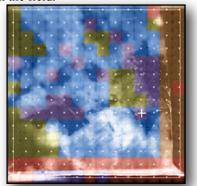
**Figure 10:** Isobar free measurement of strontium and rubidium isotopes.



Figure 11: LDRIMS 2 in Chevy Suburban.



**Figure 12:** MDA rover, Honeybee Robotics drill, and LDRIMS in the field.



**Figure 13:** μFTIR spot measurement of BCG overlain with mineralogy (blue = feldspar, purple = amphibole, quartz = yellow, standard = orange, red = edge of sample).

[2]. These methods will provide new data on E2E-iSAG priorities 1-3, 5, and 8, and reproduce the desired E2E-iSAG in-situ measurements (1-4, p.8) [3]. The approach provides insight into organic biohazards, addressing req. 2, including SKG B.2, and the chemistry of trace/minor phases that may act as, or inhibit, catalysts for ISRU (SKG B.7) [4]. These new approaches are responsive to req. 3 challenge area 1.2, "...in situ instrumentation to identify and triage high-priority materials for analysis". Finally, while meeting

many of the science goals of req.s 1-3, our mission avoids the issues of req 4. The mission may be possible as a static lander and meet req. 5, but would achieve a much higher science return with a modified MER rover. If the budget outlook improves, our payload would be ideally suited to the first MSR caching rover and meets all of the objectives of the MRR-SAG. Our mission feeds forward into MSR by validating that the collected samples are astrobiologically and geochronologically relevant, and triages those samples by scientific priority for return by MSR.

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