Methods for in situ radiometric dating on Mars with Curiosity and future landers. C.A. Malespin[1,2], P.R. Mahaffy[1], K.A. Farley[3], J.P. Grotzinger[3], P.M. Vasconcelos[4], P.G. Conrad[1], J. A. Cartwright[3], and the MSL Science Team. [1]NASA Goddard Space Flight Center, Code 699, Greenbelt, MD, 20771 charles.a.malespin@nasa.gov , [2]Goddard Earth Science Technology and Research, Universites Space Research Association, Columbia, MD, [3]Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA 91125, [4]School of Earth Sciences, University of Queensland, Brisbane, Queensland, QLD 4072, Australia

Introduction: The first in situ radiometric and exposure age dating of the Martian surface (Cumberland mudstone) was done by the Mars Science Laboratory's Sample Analysis at Mars (SAM) on Sol 355 yielding a K-Ar age of 4.21±0.35 billion years (Ga), with a surface exposure age of 78±30 million years (Ma) [1]. One of the many applications of this important result is to compare the in situ K-Ar date with that calculated from Martian crater counting. Crater counting has been controversial due to the lack of in situ geochronology to calibrate crater production rate models. These, alongside future more precise, K-Ar results may help constrain crater models.

The radiometric dating results were obtained from the pyrolysis and mass spectrometry of a drilled Martian sample, Cumberland, which was sieved and portioned into SAM for analysis. The evolved noble gas experiment was a derivative of the nominal SAM evolved gas analysis which had already been run several times on Mars [2]. Preparation for and development of this experiment were done at NASA's GSFC using the SAM high fidelity testbed. While the experiment proved successful, there is room for improved precision using more complex SAM features and future analytical techniques. Here we discuss the procedural development of the SAM measurement, and where the experiment could be improved for future landers.

SAM Testbed: The SAM instrument suite is described in detail in Mahaffy et al [3]. The SAM testbed (TB) is an identical high fidelity engineering model of the flight unit (FM). It is operated at NASA GSFC in a Mars environment chamber which reproduces the thermal and atmospheric conditions the FM unit experiences in Curiosity. All experiments are tested and verified several times on the TB prior to running on the SAM FM, which allows for generous versatility by changing and optimizing experimental parameters.

SAM TB Evolved Noble Gas: Procedures for the evolved noble gas experiment were developed and iterated over several months before running a 'blind' test solid sample to verify the final procedure. The sample was ~50 mg of a natural ~8 Ma jarosite specimen, with an independently known radiogenic ^{40}Ar concentration. The goal of the TB run was to calculate the ^{40}Ar in the sample, and to ensure the experiment was able to isolate the minor isotopes of Ar.

Figure 1 shows a simplified SAM gas flow diagram highlighting the components used in the solid noble gas experiment. The sample was heated up to ~890° C for 25 minutes after which the evolved gases were purified using a zeolite CO_2 scrubber and chemical getter. The residual gas was then leaked into the mass spectrometer in a high sensitivity scanning mode for analysis. This newly developed high sensitivity 'semi-static' mode (see supplementary material in [1]) restricts flow out of the quadrupole mass spectrometer (QMS) by partially closing the valve to the turbomolecular pump, which increases the pressure and signal intensity in the QMS. To estimate the ^{40}Ar sensitivity in the TB run we used the Mars atmospheric mixing ratio of Ar[4] and the known SAM volumes to calibrate the counts/sec of measured ^{40}Ar from the jarosite. The ^{40}Ar signal measured in semi-static mode was fairly small, but in reasonable agreement with the known abundance. This agreement adequately validated the new evolved noble gas extraction method on SAM.

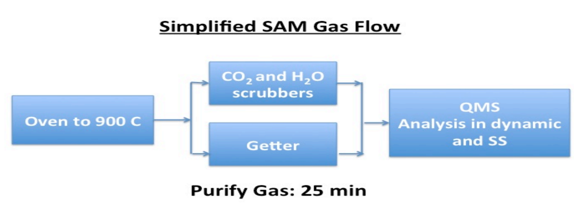

Figure 1. Simplified Gas Flow Diagram for SAM. Sample is pyrolyzed in pyro 1 and purified using a zeolite CO_2 scrubber and chemical getter to enrich the evolved noble gases before being analyzed with QMS

SAM FM Evolved Noble Gas: The evolved noble gas experiment was run on Mars on Sol 355 after minor modifications from the TB run. The mass 40 signal from the Cumberland sample consisted of both ^{40}Ar and a minor isobaric hydrocarbon. Previous measurements constrained the mass 40/mass 39 hydrocarbon ratio in SAM, so mass 39 was used as a proxy by which to isolate the ^{40}Ar signal (Figure 2). Note how m39 signal starts out very high as the QMS filament is warmed, but drops quickly to near zero implying that essentially all of the m40 signal at the end of the experiment is from ^{40}Ar. Only data from after the stabilized time interval was used for the K-Ar age determination.

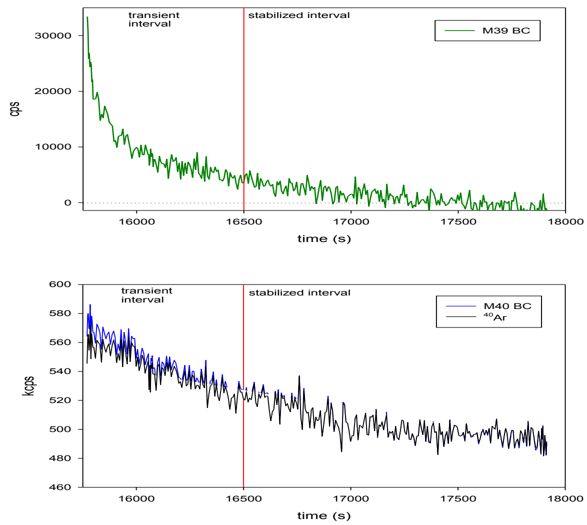

Figure 2. (Top) Mass spectrum of m39, hydrocarbon, used as proxy for HC contribution to m40. Note the rapid decline in signal. (Bottom) Mass spectrum of m40 which shows the HC contribution that quickly drops leaving residual ^{40}Ar(black)

Although ^{36}Ar is often used to correct a K-Ar age for an atmospheric Ar component, in the Cumberland sample ^{36}Ar is overwhelmingly cosmogenic in origin. Fortunately, the atmospheric ^{40}Ar component in the Cumberland sample is likely to be negligibly small [1]. Nevertheless an accurate assessment of ^{36}Ar concentration is useful for estimating the surface exposure age of the sample because it is produced by capture of cosmogenic neutrons by Cl. Since the m/z 36 signal was a combination of ^{36}Ar and $H^{35}Cl$, in order to extract the Ar signal, the HCl contribution was estimated from m/z 38 ($H^{37}Cl$), shown in Figure 3. This method was applied to each point of the mass 36 signal to calculate the residual ^{36}Ar.

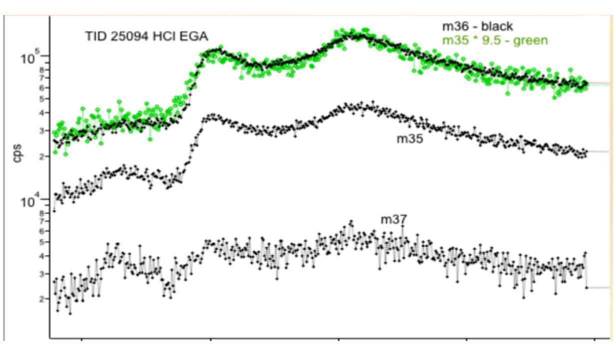

Figure 3. SAM EGA spectra vs time on previously run sample showing HCl contributions to m/z 35 and 36 with the green line scaling m35*9.5 to compare to m/z 36.

Similar independent methods were used to remove isobars for ^{3}He and ^{21}Ne, along with a full procedural blank, to yield the residual cosmogenic contribution in the Cumberland sample.

Improvements to K-Ar dating method: SAM used the standard K-Ar dating technique based on the branching decay system of ^{40}K to ^{40}Ar and ^{40}Ca. The K-Ar age equation is:

$$t = \frac{1}{\lambda} * \ln\left(\frac{\lambda}{\lambda_e} * \frac{^{40}Ar}{^{40}K} + 1\right) \qquad \text{(Eq 1)}$$

where t is the age, λ is the total ^{40}K decay constant, λ_e is the decay constant for ^{40}Ar production by electron capture, and ^{40}Ar is the radiogenic daughter product from in-situ decay. The ^{40}K half life, ($t_{1/2}$), of this decay scheme is 1.3 Ga making it ideal for dating systems spanning the entire age of the solar system. The major source of error in our current method is that it relies on accurate measurement of the sample mass. The sample mass measured by MSL, described in the supplementary material of [1], alongside uncertainty calculations for the K concentration, was the largest contributor to the ~8% uncertainty in the measured K-Ar age. If the error in the mass estimate could be eliminated, the estimated uncertainty on the K-Ar age would be ~5%.

A novel approach to K-Ar dating that removes the uncertainty in mass altogether is the double-isotope dilution K-Ar dating (ID-KArD), which is described in [5,6]. Implementation of the double-isotope-dilution method in situ on Mars would improve the precision of dating by eliminating the need for a mass determination and by making both K and Ar measurements, and isotope ratio determinations rather than concentration estimates. The method also ensures complete noble gas extraction at modest temperature (and power consumption) by using a lithium borate flux. This method could be integrated on future payloads building on the SAM evolved noble gas experiment heritage and technique. With the improved precision of isotope dilution, in situ radiometric dating could provide a critical new calibration for the Martian cratering rate.

References:[1] Farley, K. et al (2013) Science 342, Art. No 1247166. [2] Leshin, L. et al., Science 341, 1238937 (2013). [3] Mahaffy, P.R. et al (2012) Space Sci Rev. 170, 401-478. [4] Mahaffy, P. et al (2013) Science 341, 6143, pp 263-266. [5] Cartwright, J. et al (2013) LPSC 2013 abs. [6] Farley, K. et al (2013), Geochimica et Cosmochimica Acta, 110, 1-12

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