

TOWARD AN IN SITU NOBLE GAS-BASED GEOCHRONOMETRY ON THE SURFACE OF MARS: LESSONS FROM THE DEVELOPMENT OF PLANETARY MASS SPECTROMETERS. P. R. Mahaffy¹ and P. G. Conrad², ¹NASA Goddard Space Flight Center, Greenbelt, MD 20771, ²Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109.

Introduction. Recent Mars orbital missions such as the Mars Reconnaissance Orbiter (MRO) and Mars Express (MEX) have revealed locations that suggest mineralogical and morphological promise for exploration of the evolution of Mars. However, to understand the processes that have affected the martian surface requires some sense of the timing of evolutionary milestones and the detailed geochronometry that has proven so valuable in terrestrial studies has not yet been possible on Mars. Our interrogation of martian chronology is based upon measurements obtained from a handful of Mars meteorites. For example, the absolute dates of the transition from what was evidently a wetter and more chemically neutral surface environment to a volcanically dominated acidic and dryer sulfur environment [1] are not accurately known. The ages are somewhat constrained by the cratering record, but only with substantial uncertainties due to the required normalization to the lunar record. A few more precise dates at carefully selected sites on Mars might greatly constrain the duration of those critical habitability windows that could have been favorable for the potential origin of Martian microbial life and point toward optimal targets for future sample return missions that search for ancient biosignatures.

Analytical Approaches to In Situ Geochronology: Possible in situ chronometry methods include those decay pairs that require measurement of a noble gas product (U-He or K-Ar) and those that do not such as the lithophile-element chronometers (Rb-Sr, Sm-Nd, U-Pb, and Re-Os). Thermally released noble gases can be measured by a mass spectrometer using electron impact ionization and the more refractory elements by mass spectrometry following electron impact ionization or by resonance ionization time-of-flight mass spectrometry of volatilized elements. Due to the technical complexity involving both instrumentation and sample preparation requirements, there are widely diverging views on the possibility for near term success in robotic geochronology investigations. Nevertheless, in recognition of the potential high return from such experiments, NASA has supported instrument development efforts in this area for several years. Continued progress will require development of mature breadboards of candidate in situ instruments that can be demonstrated both in the laboratory and in the field using terrestrial analogs of potential target Mars surface environments. Such a campaign could demon-

strate if the precisions needed to constrain important questions for the evolution of Mars can be realized with robust and resource constrained instruments for a modest cost compared to a flight mission.

(U-Th)/He Thermochronometry: The sufficiently high U and Th abundance and the low He closure temperature have led to use of the mineral fluorapatite ($\text{Ca}_5(\text{PO}_4)_3(\text{F},\text{Cl})$) for dating of rock cooling using this system. Increased quantification from studies of He diffusivity and grain size effects has led to wider application of this technique [2] in work pioneered by these authors. This mineral is relevant to martian chronology as well having been described in SNC meteorites [3]

K-Ar geochronology: Sedimentary environments that contain minerals such as jarosite identified by the MER rovers [4] might be interesting targets for K-Ar dating. Nevertheless, the issues that have been studied extensively for terrestrial samples such as loss of Ar or K by weathering, contamination from atmospheric Ar, and on Mars, the Ar loss from impact shocks must be considered. Data from analysis of Ar in Martian meteorites has been utilized [5] to calculate precisions for in situ measurement of both Ar and Kr that would be required for a substantially improved Martian chronology. Simulated K-Ar isochrons [6] have enabled an examination of various factors such as variation in K abundance that would impact the ability to realize meaningful robotic Kr-Ar in situ dating of Martian rocks.

Noble Gases produced by Galactic Cosmic Rays (GCR): The production of ^{80}Kr , ^{36}Ar , and ^{128}Xe from neutron capture by near surface Br, Cl, and I respectively has been calculated [7]. Measurement of the abundance of these gases in regolith samples (together with the abundance of the source elements) could provide an important measure of the exposure of this material to the near surface where the GCR neutron production takes place.

Lessons on Noble Gas Measurements from Planetary Mass Spectrometer Development: Although noble gas measurements are only a part of an in situ geochronology experiment, it is useful to consider the measurement accuracy and precision that we expect to realize with a space-miniaturized instrument. The Galileo Probe Neutral Mass Spectrometer (GPMS) measured the $^3\text{He}/^4\text{He}$ ratio [8] to $\pm 3\%$ and the major isotopes of Xe to several percent [8] as it descended through the atmosphere of Jupiter. However, the

GPMS [9] operated in a dynamic sampling mode during these measurements with gas from either a direct leak to the Jovian atmosphere or gas delivered from an enrichment cell introduced to the ion source of the mass spectrometer while it was being pumped by a series chemical getter and miniature ion pump developed specifically to efficiently remove noble gases including the abundant Jovian helium. This highly miniaturized dynamic pumping system contributed to small fluctuations in the ion source density that limited the precision of the measurement. With additional time for sample analysis and processing we have implemented a static noble gas measurement capability on the mass spectrometer on the Sample Analysis at Mars (SAM) suite of instruments in the 2011 Mars Science Laboratory (MSL) rover, Curiosity. Figure 1 illustrates a highly simplified diagram of the SAM gas processing system (GPS) showing those elements necessary to make higher precision noble gas measurements.

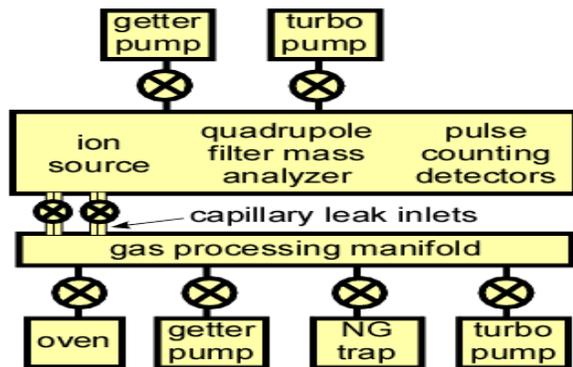


Figure 1. A simplified gas flow diagram of the SAM mass spectrometer and GPS elements relevant to noble gas measurements. Gases released in the oven from solid samples are exposed the manifold getter to remove active gases. Heavy noble gases Kr and Xe can further be separated on a trap. Small volumes of noble gases are introduced into the mass spectrometer through the capillary leaks. The mass spectrometer itself pumps active gases with its own getter while the valve to the turbomolecular pump is closed to secure a high precision static noble gas measurement.

Measurements with the Flight Model of the SAM Mass Spectrometer: During calibration of the MSL SAM quadrupole mass spectrometer we have obtained noble gas calibration data in a Mars simulation environment. The acquisition has been obtained in both a static and dynamic measurement mode. For example, Figure 2 illustrates a single mass high resolution mass scan with laboratory argon introduced to the instrument. The measured $^{36}\text{Ar}/^{40}\text{Ar}$ ratio secured with an integration time of 3.8 seconds is within about $\frac{1}{2}$ of

a percent to the terrestrial ratio. Xe and Kr measurements show similar precisions.

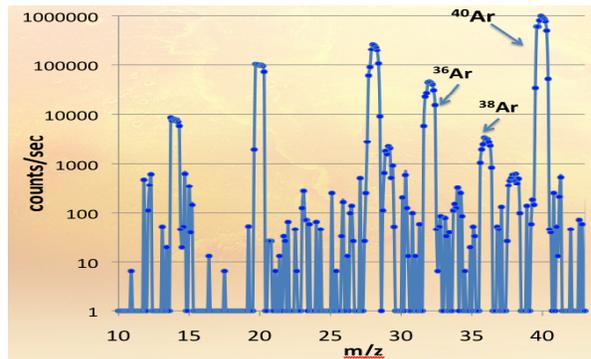


Figure 2. A mass spectrum from the SAM FM in its environmental chamber during an Ar calibration. For better precision in noble gas measurements scans are acquired at 0.1 m/z resolution instead of the more usual scan sequence that steps to the nominal peak center in a unit mass scan. The $^{36}\text{Ar}/^{40}\text{Ar}$ ratio measured in this scan is 0.00343.

Discussion: Although this discussion has focused on aspects of noble gas-based geochronology it should be noted that in addition to development of these technologies [5], active development of a laser resonance ionization mass spectrometer for Rb/Sr dating technique is ongoing [11]. Many of the elements necessary for the noble gas part of an in situ geochronology experiment have been developed and flight qualified for the MSL SAM experiment. These include gas processing and separation technologies. Further progress toward a future geochronology experiment should include development of higher temperature extraction methods than the 1100 C ovens of SAM to insure complete noble gas extraction from a variety of minerals. With future development of suitably robust companion measurements of K and U/Th it may be possible to envision a useful future noble gas-based in situ geochronology investigation.

References: [1] Bibring, J.-P., et al. (2006), *Science*, 312, 400 - 404, doi:10.1126/science.1122659. [2] Ehlers, T.A. and Farley, K.A. (2003) *Earth and Planetary Science Letters* 206, 1-14. [3] Shuster, DL & Weiss, B.P. (2005) *Science* Vol. 309. no. 5734, pp. 594 - 600 [4] Squyes, S. et al., (2006) *Science* 313, 1403-1407. [5] Swindle, T.D. (2001) *Lunar and Planetary Science XXXII*, 1492. [6] Bogard, D.D. (2009) *Meteoritics & Planetary Science* 44, 3-14. [7] Rao, M.N. et al., (2002) *Icarus* 156, 352-372. [8] Mahaffy, P.R., et al. (1998), *Space Science Reviews* 84, 251-263. [9] Mahaffy, P.R. (2000) *Journal of Geophysical Research* 105, 15061-15071. [10] Niemann, H.B et al. (1992) *Space Science Reviews* 60, 111-142. [11] Anderson, F.S. (2005) *LPSC XXXVI*, 1843.