A NEW APPROACH TO IN-SITU K-Ar GEOCHRONOLOGY. J.A. Hurowitz¹, K.A. Farley², N.S. Jacobson³, P.D. Asimow², J.A. Cartwright¹,², J.M. Eiler², G.R. Rossman², Kathryn Walterberg²,¹Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA (joel.a.hurowitz@jpl.nasa.gov), ²Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA, ³NASA Glenn Research Center, Cleveland, OH, ⁴Abteilung Biogeochemie, Max Planck Institut für Chemie, Mainz, Germany.

Introduction: The development of an in-situ geo¬
chronology capability for Mars and other planetary
surfaces has the potential to fundamentally change our
understanding of the evolution of terrestrial bodies in
the Solar System. For Mars specifically, many of our
most basic scientific questions about the geologic his-
tory of the planet require knowledge of the absolute
time at which an event or process took place on its
surface. For instance, what was the age and rate of
early Martian climate change recorded in the miner-
alogy and morphology of surface lithologies (e.g., [1])?
In-situ ages from a few select locations within the
globally established stratigraphy of Mars would be
transformative, enabling us to place direct chronologic
constraints on the timing and rates of impact, volcanic,
sedimentary, and aqueous processes on the Martian
surface.

The current paradigm for establishing absolute ag-
es on the Martian surface is through statistical methods
based on lunar crater counting techniques. Progress has
been made in previous decades, improving the preci-
sion of such estimates (e.g., [2]). However, precision is
not equivalent to accuracy, and two inescapable facts
regarding crater counting techniques remain: (1) “Any
estimate of the Martian absolute chronology involves,
implicitly or explicitly, an estimate of the Mars/Moon
cratering rate ratio” [3]; and (2) Mars is geologically
active, continually removing the record of craters and
therefore causing bias towards younger ages. Thus,
uncertainties on the accuracy of crater counting ages
can exceed a factor of 2 in portions of Martian geolog-
ic history where constraints on crater flux are particu-
larly poor. These issues will continue to cast doubt on
crater age accuracy until radiometric age tie-points are
provided for Mars.

Previous and ongoing efforts at the design of in-
situ geochronology systems have targeted precisions of
± 15-20%. The new methodology we propose for
measuring in-situ potassium-argon (K-Ar) ages has the
potential to significantly improve on this measurement
precision. Such improvements would increase the utili-
ty of in-situ ages for early Martian history, where
crater counting methods are thought to be at their most
accurate [3], and enable us to meaningfully address
rates of processes on Mars.

The Issue of Excess Ar in Shergottite Meteorites

In discussions with our colleagues it is clear that
there is a general uneasiness regarding the feasibility
of accurately K/Ar dating Martian basalts. The reasons
for this uneasiness are most clearly stated in a series of
papers by Bogard and colleagues [4-6]. The main con-
cern is that the Ar/Ar ages of the most abundant class
of SNC meteorites – the shergottites – are substantially
older than their formation ages determined from other
radiometric systems such as Sm/Nd, Rb/Sr and U/Pb.
For example, Zagami is thought to have crystallized at
170 Ma, yet its Ar/Ar “age” (depending on what phase
and what type of analysis is being considered) is more
in the range of 300 Ma (and in some cases far older)
[4]. Several studies have demonstrated that the cause
of this discrepancy is excess Ar in the shergottites.
This Ar is thought to be derived from shock implanta-
tion of atmospheric gases and from trapping of mag-
matic Ar [5, 7]. There are several reasons that we still
believe that attempting K/Ar age determinations on
Martian basalts is worthwhile:

1) Other classes of SNC’s give accurate K/Ar
ages. For example, nakhlites and Chassigny yield
Ar/Ar ages of about 1.35 Gyr, very similar to ages ob-
tained from other techniques [8]. Thus it is not clear
how pervasive this excess Ar problem really is in terms
of the surficial coverage of Mars (as opposed to in the
very unusual subset that has been launched to Earth).
Specifically the shergottites are very shocked rocks
(possibly associated with the launch event) and so may
be expected to have larger amounts of shock implanted
gases than typical surface basalts.

2) Bogard et al. [5] make the very curious obser-
vation that the amount of excess Ar in Shegottite min-
eral fractions is rather constant in their analyses, about
1x10⁻⁶ cm³ STP of ⁴⁰Ar. This is important because in a
basalt with a typical shegottite K concentration this is
equivalent to about 200 Myr of Ar accumulation (i.e.,
the K/Ar age would be about 400 Myr instead of the
“true” age of most shegottites of ~200 Myr). However
in a 2 Gyr basalt with the same K content and amount
of excess Ar, the excess would yield just a 6% error in
age (and this reduces to just 2% in a 3.5 Gyr basalt).
In other words, the fact that the shergottites are so young
is what makes this effect so noticeable. In our opinion
an error of this magnitude is acceptable, since the frac-
tion of extremely young basalts (<500 Myr) on the
surface of Mars is almost certainly very low.

3) Bogard [6] notes the difficulty of obtaining
the very high temperatures necessary to completely
extract Ar from basaltic melts. Because we employ a
flux-assisted digestion technique this issue is not rele-
vant to our proposed approach (see below).
A New Approach to K-Ar Geochronology: We recognize that there are two major technical hurdles to making an accurate and precise in-situ K-Ar age measurement: (1) achieving melting temperature for rocks in order to quantitatively degas them of argon, and (2) measuring sample mass as a means of relating K-concentration to absolute abundance of argon. Here, we describe a new approach to in-situ measurement of K-Ar ages that solves both of these problems simultaneously.

In broad terms, our measurement protocol involves four steps. In step 1, a crushed or powdered sample is delivered to a crucible in a vacuum chamber, which has been loaded on Earth (i.e., prior to flight) with a lithium-based fluxing agent and a solid double-spike containing known amounts of isotopically enriched isotopes of 39Ar and 41K. The \( \frac{39\text{Ar}_{\text{spike}}}{41\text{K}_{\text{spike}}} \) ratio is thus known, forming the basis of our age calculation (see below). In step two, the sample-flux-spike mixture is melted by heating the crucible with resistance heaters. The flux agent contains LiBO\(_2\), which melts at 849°C and Li\(_2\)B\(_4\)O\(_7\), which melts at 920°C. Heating to temperatures between 950-1000°C therefore readily achieves melting and isotopic homogenization of the sample-spike-flux mixture. In step three, the ratio of radiogenic 40Ar from the sample over 39Ar from the spike is measured on a mass spectrometer. Argon is quantitatively outgased by melting of the sample, allowing us to solve for radiogenic 40Ar in the sample by measurement of the equilibrated sample/spike ratio. In the final step (4), the \( \frac{39\text{K}_{\text{Sample}}}{41\text{K}_{\text{spike}}} \) ratio is analyzed via Knudsen Effusion Mass Spectroscopy (KEMS, [9]), using the same mass spectrometer as that used for the Ar-isotopic measurement. The measured K- and Ar-isotopic ratios are then used to solve for a whole rock age. We have validated each of the individual steps in this analytical procedure, as described below.

Calculating K-Ar Ages using Double Isotope Dilution: The K/Ar age equation is:

\[
t = \frac{1}{\lambda} \ln \left( \frac{40\text{Ar}^*}{40\text{K}} + 1 \right)
\]

where \( \lambda \) is the total 40K decay constant, \( \lambda_e \) is the decay constant for the electron capture decay mode that produces 40Ar, \( t \) is the K/Ar age, and 40K and 40Ar* are abundances in atomic units. 40Ar* is the radiogenic daughter product, and is thus the 40Ar attributable to in-situ radioactive decay. Thus an age determination requires measurement of the 40Ar*/40K ratio.

K consists of three isotopes, with masses of 39 (93.3%), 40 (0.0117%), and 41 (6.73%). For isotope dilution K measurements, 41K of high isotopic purity (>99%) is readily available. There are three stable isotopes of Ar (of masses 36, 38, and 40) and isotope dilution is usually done using 38Ar as a tracer. Since 38Ar is a useful indicator of cosmic ray exposure, we consider instead the use of synthetic 39Ar. This radioactive isotope has a half-life of 269 years and is routinely produced by neutron irradiation of 39K bearing substances.

When a spike containing the isotopic tracers 41K and 39Ar is added to the sample, and the combination fused to release and measure Ar isotopes and K-isotopes, the \( \frac{40\text{Ar}^*}{40\text{K}} \) ratio can be determined as follows (all variables are as defined in Table 1).

<table>
<thead>
<tr>
<th>Table 1. Definition of Variables</th>
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<tbody>
<tr>
<td>( \text{40Ar}^* ) &amp; in situ produced radiogenic Ar amount (unknown)</td>
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<tr>
<td>( \text{39Ar}<em>{\text{spike}}, \text{40Ar}</em>{\text{spike}} ) &amp; amount of Ar isotope in spike</td>
</tr>
<tr>
<td>( \text{40Ar_m}, \text{36Ar_m}, \text{39Ar_m} ) &amp; measured Ar amounts</td>
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<tr>
<td>( \text{40Ar}<em>{\text{air}}, \text{36Ar}</em>{\text{air}} ) &amp; air-derived argon amounts</td>
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<tr>
<td>( R_{\text{spike}} = \frac{\text{40Ar}<em>{\text{spike}}}{\text{39Ar}</em>{\text{spike}}} ) &amp; independently determined</td>
</tr>
<tr>
<td>( R_{\text{nat}} = \frac{\text{40Ar}<em>{\text{nat}}}{\text{39Ar}</em>{\text{nat}}} ) &amp; natural K isotopic composition (known)</td>
</tr>
<tr>
<td>( R_{\text{air}} = \frac{\text{40Ar}<em>{\text{air}}}{\text{36Ar}</em>{\text{air}}} ) &amp; known</td>
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First, for Ar:

\[
\text{40Ar}_m = 40\text{Ar}^* + 40\text{Ar}_{\text{air}} + 40\text{Ar}_{\text{spike}} \quad (1)
\]

\[
\text{36Ar}_m = 36\text{Ar}_{\text{air}} \quad (2)
\]

\[
\text{39Ar}_m = 39\text{Ar}_{\text{spike}} \quad (3)
\]

Where equation (1) is the mass balance for 40Ar and indicates that some of the 40Ar is derived from “contamination” with (terrestrial or martian) atmospheric argon. The second and third equations indicate that all 36Ar is air-derived and all 39Ar is spike-derived. Combining these equations and the definitions in Table 1 yields:

\[
40\text{Ar}^* = \left( R_m - R_{\text{air}} \frac{36\text{Ar}_{\text{air}}}{39\text{Ar}_{\text{air}}} \right) - R_{\text{spike}} 39\text{Ar}_{\text{spike}} \quad (4)
\]

In the case of K:

\[
39\text{K}_m = 39\text{K}_{\text{u}} + 39\text{K}_{\text{spike}} \quad (5)
\]
Where equations (5) and (6) reflect mass balance and equation (7) states that the isotopic composition of the unknown sample is that of natural potassium. Combining these equations and the definitions in Table 1 yields:

\[ ^{40}K_u = r_{40} \left( \frac{r_{spk} - r_{alt}}{r_{alt} - 1} \right) ^{41}K_{spk} \]  

Combining equations 4 and 8 yields the ratio from which the K/Ar age is determined:

\[ \frac{^{40}Ar}{^{39}Ar} = \frac{r_{alt} - r_{40} \left( \frac{r_{spk} - r_{alt}}{r_{alt} - 1} \right) - r_{spk} \left( r_{spk} - r_{40} \left( \frac{r_{spk} - r_{alt}}{r_{alt} - 1} \right) \right)}{r_{alt} - r_{40} \left( \frac{r_{spk} - r_{alt}}{r_{alt} - 1} \right)} \]  

It is important to note that by using equation 9, the K/Ar age can be computed directly from measured isotopic ratios without knowledge of the mass of the sample or of the spike glass. This is a fundamental advantage of our age-dating technique, and is built on the fixed \(^{39}Ar_{spk}/^{41}K_{spk}\) ratio. Furthermore, because we only require the measurement of isotopic ratios with our technique, instrument calibration becomes much simpler or possibly even unnecessary.

**Synthesis of a Double Isotope Spike:** We have prepared an alkali-feldspar glass that contains the isotope dilution spikes \(^{41}K\) and \(^{39}Ar\). The glass was prepared in a 2-step synthesis procedure. In the first step, pure oxide (SiO\(_2\), Al\(_2\)O\(_3\)) and carbonate (Na\(_2\)CO\(_3\)) components were fused at 1150°C in a Pt-crucible in an open-tube gas mixing furnace to form a melt. This melt was held above the liquidus for ~48 hours and then quenched to form albite glass (NaAlSi\(_3\)O\(_8\)). The product glass was then crushed with a mortar and pestle and mixed with KCl (obtained from the Oak Ridge National Laboratory) that is enriched in the \(^{41}K\) isotope (99.17% \(^{41}K\)). This mixture was also loaded in a Pt crucible and fused at 1150°C into an open-tube gas mixing furnace that was continuously purged with a CO\(_2\)-H\(_2\) gas mixture. The gas mixture was “tuned” to maximize pH\(_2\)O at 1150°C and remove Cl from the mixture as HCl vapor, leaving the K in the melt. Experiments at low pH\(_2\)O revealed that K is quantitatively lost from the melt owing to the relatively high volatility of KCl. The melt was held above the liquidus for ~96 hours and then quenched to form a glass. Electron microprobe analysis of this glass indicates typical K\(_2\)O\(_{total}\) concentrations of 6-8 wt%. Because the KCl contains a trace of \(^{39}K\) (<0.83%), the glass can be neutron irradiated using typical Ar-Ar irradiation conditions. This produces \(^{39}Ar\) in the glass by neutron capture, yielding our final double-isotope solid spike. Our synthetic glass was subjected to neutron irradiation for ~50 hours in the Oregon State University TRIGA reactor.

**Argon Isotopic Measurements:** We have performed a variety of experiments designed to measure the Ar-isotopic composition of gases released from silicate materials fused in the presence of a Li-based fluxing agent (50% Li-metaborate, 50% Li-tetraborate). In early experiments, a K-feldspar sample was mixed with a SrCl tracer, in order to determine whether flux-assisted digestion of silicate minerals results in argon release at low temperatures (1000°C), and whether or not sample-tracer homogeneity is achieved by flux-assisted digestion. The results shown in Fig. 1 indicate that Ar-release occurs during flux digestion. In addition, laser ablation ICP-MS analysis of the glass produced during this experiment has a homogeneous K/Sr ratio (not shown), demonstrating sample-spike equilibration during flux-assisted melting.

**Fig. 1:** \(^{40}Ar/^{36}Ar\) isotope ratio of K-feldspar measured as a function of time on a quadrupole mass spectrometer during flux-assisted digestion. The \(^{40}Ar/^{36}Ar\) ratio is significantly elevated relative to atmospheric \(^{40}Ar/^{36}Ar=296\), indicating release of radiogenic \(^{40}Ar\) (i.e., \(^{40}Ar^*\)) from the sample.

In subsequent experimentation, we mixed a 132 Ma basalt obtained from the Paraná basin of Brazil with our double-isotope spike and flux-melted the mixture at 1000°C. This yielded measurements of 60% radiogenic Ar from this young, low-K (<0.5 wt % K\(_2\)O) basalt.
Potassium Isotope Measurements with KEMS: We have performed a series of experiments at the NASA Glenn Research Center that were designed to determine whether the application of KEMS could provide a suitable means of measuring the K-isotopic composition of vaporized K during low-temperature flux-assisted melting. Briefly, KEMS involves melting of the sample in a specially designed cell (in our case, made of Mo), production of a vapor that exits the top of the crucible in the Knudsen flow regime, line of sight ionization of neutral vapor species, and measurement of the ionized isotopes on a mass spectrometer, in our case a magnetic sector instrument [9]. The high resolution of the magnetic sector instrument allows separation of the $^{39}$K peak from background hydrocarbons, and hence more accurate measurements.

Our experimental results are shown on Fig. 2, which is a plot of measured $^{39}$K as a function of temperature for: (1) Parana basalt, (2) Parana basalt melted in the presence of flux, (3) non-isotopically enriched spike glass melted in the presence of flux, and (4) flux as a control. The salient results of these experiments can be summarized as follows: KEMS provides long lived (2-3 hours), stable $^{39}$K signals from all of the analyzed samples (except for the control, which contains no measureable K); K measurements can be made at low temperature (<1000°C) during flux assisted melting, (3) the onset of K-vaporization occurs at the same temperature for both the spike glass and the basalt during flux-assisted melting, indicating that equilibration of K-isotopes from sample and spike should be readily achievable.

Future Work: Presently, we are synthesizing a second batch of an isotopically-enriched spike that will be used to produce our first age measurement using the methodology we have developed. This will be accomplished in a 2-step procedure in which a mixture of flux, Parana basalt, and spike glass are combined in a Knudsen cell crucible and melted in a furnace attached to a noble gas mass spectrometer in the Geological and Planetary Sciences Department at Caltech. The gases released following melting will be analyzed to measure the Ar-isotopic composition. The melt will then be quenched, and the Knudsen cell crucible containing the glass will be sent to NASA Glenn Research Center for measurement of the K-isotopic composition of the glass using a KEMS instrument. From these isotope ratio measurements, the age of the Parana basalt sample will be computed.

Once we have successfully demonstrated an end-to-end age measurement using this technique, we will begin the construction of a single benchtop instrument that can accomplish the entire measurement in a single-step melting procedure. Due to the simplicity of our measurement technique, the benchtop instrument system will be relatively straightforward to build and operate. Essentially what we require is a resistance furnace, a line-of-sight ionizer, standard plumbing for enrichment and sequestration of noble gases, and a small mass spectrometer capable of measuring isotope ratios. From this basic benchtop architecture, we can design a suitably miniaturized instrument system for field testing and eventual flight prototyping.

In summary, we have developed an inherently simple experimental methodology that can be employed for the measurement of K-Ar whole rock ages on the surface of Mars, the Moon, and other Solar System bodies of interest. Our technique requires neither high fusion temperatures for Ar-release, nor a means of weighing aliquots of sample to relate K-concentration to Ar-abundance; both of which have been significant technical hurdles that have hampered previous attempts to produce in-situ instruments for K-Ar geochronology. This technique is applicable to materials with low-K concentrations, and requires only the measurement of isotope ratios, making in-flight mass spectrometer calibration simple or perhaps even unnecessary.

Fig. 2: $^{39}$K signal measured on the NASA Glenn Research Center KEMS as a function of temperature. Note that the onset of $^{39}$K signal for flux assisted melting of basalt and spike occurs at 845°C, which is the melting point of the Li-metaborate flux.