Instrumentation development for planetary in situ $^{40}Ar/^{39}Ar$ geochronology

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Abstract

The chronology of the Solar System, particularly the timing of formation of extraterrestrial bodies and their features, is a major outstanding problem in planetary science. Although various chronological methods for in situ geochronology have been proposed (e.g. Rb-Sr, K-Ar), and even applied (K-Ar, Farley et al., 2014), the reliability, accuracy, and applicability of the $^{40}Ar/^{39}Ar$ method makes it by far the most desirable chronometer for dating extraterrestrial bodies. The method however relies on the neutron irradiation of samples, and thus a neutron source. Herein we discuss the challenges and feasibility of deploying a passive neutron source to planetary surfaces for the in situ application of the $^{40}Ar/^{39}Ar$ chronometer. Requirements in generating and

shielding neutrons, as well as analyzing samples are described, along with an exploration of limitations such as mass, power, and cost. Two potential solutions for the in situ extraterrestrial deployment of the $^{40}Ar/^{39}Ar$ method are presented. Although this represents a challenging task, developing the technology to apply the $^{40}Ar/^{39}Ar$ method on planetary surfaces would represent a major advance towards constraining the timescale of solar system formation and evolution.

1. Introduction

1.1 Planetary timescales

Accurate and precise determination of timescales is critical to understanding the history of planetary and asteroidal bodies and is essential to mission planning and the search for extraterrestrial life. Extraterrestrial chronologies have been determined to some extent by isotopic analyses of meteorites from Mars and other bodies. Although the planetary or asteroidal parent body of meteorites can often be determined, the exact geographic provenance location is difficult, if not impossible, to ascertain. Thus age constraints on specific planetary surfaces have thus far been limited to relative techniques such as crater counting, which is not only reliant on calibrations to lunar cratering models (Ivanov, 2001) and the analysis of the limited samples returned from Apollo and Luna missions but is dependent on observations and assumptions of the counted surface's complex geologic history (e.g., resurfacing and exhumation). Furthermore, crater counting involves significant human interaction and errors that are often not systematic and are not easily quantified (Robbins et al., 2014).

Given the success of recent unmanned missions to Mars (e.g., Spirit, Opportunity, Curiosity), development of an *in situ* absolute dating instrument packages for future robotic missions is a logical next step (Cassata, 2014; Farley et al., 2014). Although several ongoing programs of research are developing innovative methods for the *in situ* application of the K-Ar technique (Cho et al., 2012; Cohen et al., 2014a; Cohen et al., 2014b; Farley et al., 2013; Swindle et al., 2003; Talboys et al., 2009) and other methods (Anderson et al., 2012), the

nature of the K-Ar method means that these approaches could deliver ages with questionable geologic meaning due to the likelihood of disturbed thermal histories (Figure 1). This has in particular proven true for lunar samples from the Apollo missions (McDougall and Harrison, 1999; Turner, 1970a; Turner, 1970b) and the unrecognized presence of excess ^{40}Ar.

These potential issues can be circumvented by the application of the ^{40}Ar/^{39}Ar variant of K-Ar geochronology (Cassata, 2014; Li et al., 2011; Merrihue and Turner, 1966). The ^{40}Ar/^{39}Ar technique allows for the identification of and correction for variable trapped components (e.g., excess ^{40}Ar) and resolution of complex thermal and diffusive histories. However, the method relies on the fast neutron-induced ^{39}K(n,p)^{39}Ar reaction (transmutation of ^{39}K to ^{39}Ar) so that ^{39}Ar can be measured as a proxy for the parent element K, which typically occurs in a ^{235}U fission reactor. Although the development of a ^{235}U fission reactor for spaceflight has previously been explored via the cancelled Prometheus project, the feasible option of exploiting passive neutron sources is explored herein. Within this contribution we explore the many parameters involved in deploying an instrument package for in situ ^{40}Ar/^{39}Ar geochronological analyses on extraterrestrial surfaces.

1.2 ^{40}Ar/^{39}Ar geochronology

The K-Ar and ^{40}Ar/^{39}Ar methods rely on the radioactive decay of ^{40}K to ^{40}Ar and are most often applied to high temperature igneous and metamorphic mineral phases and rocks. They are founded in the concept that ^{40}Ar atoms produced within a system are only retained when temperatures are sufficiently low to prevent diffusive loss. Typical K-Ar analyses are hampered analytically by the necessity of measuring ^{40}K and ^{40}Ar on separate aliquots, in addition to a mass measurement on each aliquot; many of these analytical issues have been potentially ameliorated with a pioneering technique designed for spaceflight by Farley et al. (2013). However, the ^{40}Ar/^{39}Ar method has a number of analytical and practical benefits over the K-Ar method. Most critically, the measurement of ^{39}Ar as a proxy for the parent isotope ^{40}K allows for incremental heating of samples and thus interrogation of thermal histories, which is required given the impact features of the planets, moons and asteroidal bodies

throughout the Solar System. Incremental step-heating data, where a sample has been heated to consecutively higher temperatures over the course of an analysis sequence, can be inspected on an age spectrum (Figure 1), where the fraction of total ^{39}Ar released is shown against the age calculated for each step. Thus portions of the age spectrum can be interpreted to represent (and determine a reliable age for) various events in the geological history of the sample, and/or indicate the presence of various complications that can occur in samples, such as excess argon and recoil effects.

One requirement of the $^{40}Ar/^{39}Ar$ method is the creation (transmutation) of sufficient quantities of ^{39}Ar from ^{39}K so that precisely measurable $^{40}Ar/^{39}Ar$ ratios are obtained. High precision measurements require $^{40}Ar/^{39}Ar$ ratios relatively close to 1, although ratios of 10 to 100 are routinely measured in terrestrially-sourced samples to limit irradiation time and costs. Older rocks, such as those found on extraterrestrial surfaces, contain more ^{40}Ar ingrown from ^{40}K and thus require larger quantities of ^{39}Ar to be created during irradiation. It is not uncommon during the analysis of meteorites for scientists to be measuring $^{40}Ar/^{39}Ar$ ratios of 300 or even higher (e.g. Bogard and Garrison, 2003). In an *in situ* extraterrestrial situation with a limited neutron flux limited by design constraints, achieving sufficient neutron fluence to create measureable $^{40}Ar/^{39}Ar$ values in reasonable timeframes becomes a difficult task. The parameters requiring consideration are discussed herein.

1.3 Sample availability and selection

The potential utility of inclusion of the system described herein to a future spaceflight mission is largely dependent on the destination of that mission. The K-Ar and $^{40}Ar/^{39}Ar$ chronometers are, by far, most applicable to igneous and metamorphic rocks, as it records the cooling age and/or thermal history of a sample. The appropriate geological interpretation of recent applications of the K-Ar method to fine sediments on Mars remains elusive, as the age represents the mean thermal history of a large number of grains and cannot be interpreted as a sedimentation age. The $^{40}Ar/^{39}Ar$ method is thus most powerfully applied in the solar system

to volcanic and/or impacted rocks; this could include those from other solid planets (e.g. Mars), moons, or smaller asteroidal bodies.

1.3.1 Calibrating Martian crater-counting chronologies

Among the most powerful potential applications of the methods presented here would involve a mission to one of the large igneous provinces on Mars, with the purpose of dating samples across these regions to calibrate crater-counting methods. Crater-counting is currently calibrated using the assumption of equivalent impact histories for Mars and the moon (Ivanov, 2001), which is itself calibrated by chronological analyses of samples returned from Apollo missions. Direct calibration of the Martian impact history would require careful selection of possible sites for dating. The relatively young, Late Hesperian to Amazonian-age (< 3.0 Ga) flood lava fields of Tharsis and/or Elysium (Tanaka et al., 2014) are ideal targets. Here, diagnostic lava morphologies (e.g., lobate flow features, lava tubes, channels) are obvious, and the areal extent (>100 – 1000 km2) of individual large flood lava flows provides a statistically significant sample of impact craters (e.g. hundreds) to robustly test the dating technique against the impact crater chronology data (Warner et al., 2015). Furthermore, Hesperian to Amazonian-age surfaces have not been exposed to the high impact rate (Hartmann and Neukum, 2001; Ivanov, 2001) or the high erosion rates (Golombek et al., 2006) that characterized the Late Heavy Bombardment period of the Late Noachian epoch. During this time, significant impact gardening and active surface processes (e.g. fluvial and aeolian activity) likely re-worked the upper tens to hundreds of meters of the Martian crust, which would challenge in-situ identification of an in-place igneous sample (Hartmann et al., 2001; Hartmann and Barlow, 2006).

Ideally, a mission could, for example, aim to land a rover at a geologic contact of Early Amazonian lava plains and the older Hesperian-age ridged plains. Such a location is available at several locations in the northern lowlands proximal to the Elysium volcanic province. The Hesperian-age ridged plains here (Tanaka et al., 2014) have been proposed to also represent flood lavas, where the thin, individual flow margins have been blended through

3+ billion years of meter-thick regolith development. In places where the regolith is only meters thick, fresh, rocky ejecta impact craters may provide windows into the near surface primary volcanic stratigraphy. It may also be possible to capture all three geologic epochs within a landing region that could be reasonably traversed by a rover along the planetary dichotomy in southern Elysium Planitia. The ultimate goal of such a mission would be to remove potential biases involved in the derivation of age on Mars using crater counts. This would significantly improve our ability to constrain the chronology of landforms and terrains across the entire surface, including those areas being explored for signs of life by Curiosity, the Mars 2020 mission, and the ExoMars mission.

1.3.2 Other potential uses of technology

A critical goal of the forthcoming Mars 2020 mission will be to collect a cache of samples for their eventual return to Earth. In the event that this return mission is impeded by significant delays, a lander mission to the site of the sample cache could be deployed to analyze samples from the cache on Mars. Similarly, the technology described herein could also be deployed on a lander or rover mission to asteroids and other solid planetary bodies whose surfaces are dominated by igneous processes (e.g., the Moon). Further, plans for future sample return missions from Mars will include sample containment facilities and protocols. If samples are to remain within a closed facility, the neutron source technology described herein could be installed to allow for in house sample irradiation. In this case, shielding requirements would be significantly higher, but mass restrictions significantly less stringent. Alternative neutron sources for this application are D-D type neutron sources (Renne et al., 2005), D-T neutron sources, and other reactor irradiation facility such as the OSU TRIGA reactor or HFIR at ORNL.

2. Sampling and sample handling

Samples for $^{40}Ar/^{39}Ar$ geochronology can be in the form of rock chips as small as 100μm, limited by the increased effects of nuclear recoil on small grain sizes. Samples of this size are

most readily collected by drilling, which can take two forms, core drilling and powder drilling, both of which have undergone development for other extraterrestrial exploration purposes.

2.1 Core drilling

Sampling and encapsulation of larger rock fragments in the form of a core can be achieved in a single process if the sample is extracted within the cutting bit and the bit is subsequently sealed. Coring bits with a centre drill can produce toroidal core samples, and ultrasonic-percussive drilling techniques can produce core samples that need not necessarily exhibit rotational symmetry. These options raise the possibility of packing bespoke sample capsules around the neutron source made from material with a small cross section for fast neutron capture, thus maximizing the neutron activation of ^{39}K.

2.2 Powder drilling

An alternative to core drilling is powder drilling. In this case, grain sizes may be sorted by sieving prior to analysis, but high-amplitude vibration that could be damaging to the instrument package is not necessarily required. Ultrasonic actuation of the sieves and associated chutes can agitate and aid transport of the material in a manner similar to that currently employed on the CheMin instrument. The receiving hopper associated with each sieve may then be shaped and employed as a sample capsule, as with the core drilling methods. Ideal grain sizes are 250-500µm.

3. Neutron generation

Although terrestrial application of the $^{40}Ar/^{39}Ar$ method typically relies on neutrons produced by a ^{235}U fission reactor, the deployment to planetary surfaces of a reactor at nuclear criticality is unlikely. The approach taken here, similar to that of Li et al. (2011), instead involves a transport and exploitation of a passive neutron source. The most viable passive neutron source is ^{252}Cf, with its relatively high neutron flux by mass (ca. $2.33x10^9$ n/s for each mg of

material) and relatively low specific heat output compared with other passive neutron sources (Table 1). Challenges in deploying this source are (1) it has a relatively short $t_{1/2}$ of 2.645 years, and (2) ^{252}Cf is difficult to produce; as of the year 2000 the High Flux Isotope Reactor (HFIR) at Oak Ridge National Laboratory (ORNL) typically produced ca. 250 mg per year (Martin et al., 2000). Obtaining sufficient neutron fluences from reasonable quantities of source material over reasonable irradiation durations is a major limitation and is addressed herein.

The required neutron flux for sample irradiation depends largely on the abundance of K and the sample age (amount of radiogenic ^{40}Ar). Terrestrially, a ^{40}Ar/^{39}Ar ratio of 100 on a 4 Ga sample can be obtained, for example, by a 13.6 day irradiation in the fast neutron flux of 2.47×10^{13} n/cm^{2}s in the CLICIT Facility of the Oregon State University TRIGA Reactor (see Figure 2). This yields a total neutron fluence of 2.90×10^{19} n/cm^2. In comparison, the entire 40 mg of ^{252}Cf made in some production runs at ORNL would yield ca. 1×10^{11} n/s, resulting in a neutron flux (at 1 cm distance from the source) of just ca. 8×10^{9} n/cm^{2}s, over three orders of magnitude lower than the OSU reactor. However, this is very slightly ameliorated by the neutron energy spectrum for ^{252}Cf, which is somewhat faster than that of ^{235}U fission and thus improves the efficiency of the ^{39}K(n,p)^{39}Ar reaction (Figure 3).

It is possible to increase the neutron flux via the use of neutron booster material. This is due to the fact that some materials undergo neutron-emitting reactions when exposed to a neutron source. For example, the reactions ^{9}Be(n,2n)^{8}Be, and ^{9}Be(n,3n)^{7}Be, along with the neutron-induced fission reactions on ^{233}U, ^{235}U, ^{239}Pu, ^{240}Pu, and ^{241}Pu, all emit more neutrons that required for the reaction. Below we explore the use of ^{252}Cf and the potential for neutron flux booster material as a means of increasing the neutron flux to limit the irradiation duration and achieve acceptable ^{40}Ar/^{39}Ar ratios that facilitate reasonably precise age determinations (Figure 2).

3.1 Simple ^{252}Cf source geometry

The simplest neutron source geometry considered here includes a point source of ^{252}Cf, surrounded by a space for samples and reflective shielding material (Figure 4a). Monte Carlo Neutron Particle (MCNP5) modeling shows that the neutron energy spectrum within the sample chamber (Figure 5) is relatively fast, with a fast peak in the MeV range, reflecting the neutron energy spectrum of fission-born neutrons. The Y-axis in Figure 5 normalizes the flux to units of lethargy, which accounts for the scattering efficiency of the incident material.

3.2 Complex multiplier geometries

3.2.1 Complex spherical geometry

Spherical geometries that include concentric spheres with a ^{252}Cf point source at the center surrounded by a void for samples, booster/multiplier material, and shielding were explored (Figure 4b). A spherical design should yield the most efficient boost per unit mass, relative to the complex cylindrical geometries described below. Several booster materials were considered as neutron multiplier materials, including ^{9}Be, ^{233}U, ^{235}U, ^{239}Pu, ^{240}Pu, and ^{241}Pu. We use a spherical geometry as shown in Figure 4b, with 90% enriched ^{235}U and 100% enrichment for other transuranic metal oxides and Premadex® as a reflector material. Modeling indicates that the most efficient multipliers are ^{239}Pu and ^{241}Pu, as shown in Figure 17.

3.2.2 Complex cylindrical geometry

Here, a more complex cylindrical geometry is explored, along with rotatable or extractable ‘pins’ composed of neutron multiplicative material (e.g. ^{9}Be, ^{233}U, ^{235}U, ^{239}Pu, ^{240}Pu, ^{241}Pu) and backed by neutron absorbing material (Figure 4c). This arrangement allows for a somewhat ‘switchable’ source, where the flux is enhanced when fissionable material faces the source and depressed when the ‘pins’ are rotated and absorbent material faces the source. Given sufficiently high multiplicative effects, this could serve to boost the neutron flux so that irradiation could occur in a reasonable time period (see Figure 2 below for values) while reducing the total neutron fluence seen by other instruments in the mission. This geometry

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may also be utilized to maintain a constant neutron flux over the course of a mission, as the decay of ^{252}Cf decreases the flux from the ^{252}Cf source itself.

4. Neutron shielding

Neutron shielding is important to prevent radiation damage to the rover or lander system and potentially also to prevent irradiation of the extraterrestrial surface. Neutron shielding requirements are ultimately limited by rover tolerances to an elevated neutron flux. Estimations of acceptable neutron flux tolerances for the current Curiosity rover mission are considered sensitive material by International Traffic in Arms Regulations (ITAR) and thus have not been accessible. However, some indication as to acceptable fluxes can be derived both from experiments included with the Curiosity mission and from the most sensitive components included in that mission. Towards this, the Dynamic Albedo of Neutrons Pulse Neutron Generator (DAN-PNG) experiment, which is designed to search for hydrogen, and thus water, on the surface and subsurface of Mars, emits short (1 μs) but high-energy (14 MeV) pulses of 10^7 neutrons (Litvak et al., 2008; Mitrofanov et al., 2005; Mitrofanov et al., 2012). A further constraint can be estimated based on the CCD (charge coupled device) image sensors on Curiosity from Teledyne DALSA in collaboration with NASA and should be among the most neutrons sensitive components on Curiosity. These CCD devices are radiation hardened and are designed to tolerate neutron fluxes up to $1x10^7$ n/cm^{2}s (personal communication, David Head, Teledyne DALSA), which provides a starting point for shielding calculations. Actual required shielding will depend on the allowed tolerances for future missions, which will likely be less stringent than those assumed here, and information is provided here to allow for recalculation based on those limits.

The effects of neutron flux on the system are complex, and several of these must be considered. For example, secondary effects can create radioactive elements due to the neutron irradiation of elements present in the system (e.g. Fe). Further, neutron irradiation of sensitive electronics components can affect the system in multiple ways, including first order displacement of atoms due to neutron bombardment and single-event digital effects on

semiconductor materials. The magnitude of these effects is dependent in part on the energy spectrum of the field, and selection of shielding materials will need to consider this. A future consideration would also incorporate shielding of the high-energy photons yielded by ^{252}Cf fission products. An additional consideration for shielding involves mitigating activation of the shield and rover material by the source neutrons. .

4.1 Shielding materials

Neutron shielding materials considered here include high-density polyethylene (HDPE), B_4C, Premadex®, ^{6}Li-enriched Premadex®, and Gd. These materials can act to either scatter and decrease neutron energy, e.g. HDPE and Premadex®, or to absorb neutrons by nuclear reaction, e.g. B_4C, Gd, Cd, and Li. The relative efficiencies of these materials are provided in Figure 8 and include neutrons with an energy spectrum from a ^{252}Cf fission source. Shield efficiency is considered here as a "fraction of remaining neutrons" and importantly does not consider geometric effects, which further decrease the effective flux by the square of the distance away from the neutron source and are considered separately.

4.2 Shielding a simple ^{252}Cf source

To better understand the energy spectrum of neutrons exiting shield material, the simple spherical source (Figure 4a) is modeled using 30 cm of HDPE as a shield. The energy spectrum of neutrons exiting the shield is provided in Figure 5. Note that many neutrons exiting the shield are thermalized to 10^{-7} - 10^{-8} MeV, which represent neutrons that have been downscattered, or moderated, in the shield from fast to thermal energies. Figure 8 shows the fraction of remaining neutrons in the system across the shield, for (a) various materials and (b) several composite shields. The most efficient shield would likely include a moderator to thermalize neutrons, with foils of a strong neutron absorber (e.g. Cd or Gd) with a high thermal neutron capture cross section to remove the thermalized neutrons.

4.3 Geometric effects

Geometric effects aid neutron flux mitigation by the inverse square rule; the reduction in flux due simply to distance from source (and not including attenuation due to shielding) follows the inverse square of distance. The relative effect is such that a source with a 10^{11} n/cm^{2}s flux at the sample chamber would decrease to $4x10^7$ n/cm^{2}s at 50 cm distance from the source. Further, the amount of shielding required can also be decreased due to geometric effects, if one considers shielding only the rover and not the planetary surface and/or atmosphere. For example, a neutron source located at 1 meter distance from a 1 meter square region of sensitive components would only need to cover ca. 6% of the surface area of the source.

5. Radiation, launch clearance, and planetary protection

The inclusion of a neutron source in an instrument suite for planetary exploration creates numerous safety considerations, for humans, other instruments, and planetary protection. The ^{252}Cf source would need to be added late in the manufacturing process, not only for human safety concerns but also due to its relatively short $t_{1/2}$ and thus significant decrease in neutron flux with time. Appropriate shielding would be required during installation and launch to maintain acceptable human safety conditions.

The possibility of a catastrophic launch must also be considered. The neutron source in particular needs to be encased so that it retains radioactive material during a launch failure situation. Further, the inclusion of any fissionable booster material in the source must remain below criticality levels in any accident scenario, including the case of potentially high pressures experienced during a crash landing situation. The potential for long-term radioactive contamination is low due to the relatively short $t_{1/2}$ of ^{252}Cf, but daughter products may also be problematic. In particular, spontaneous fission (SF) produces various unpredictable daughter isotopes, and alpha decay produces ^{248}Cm ($t_{1/2}$ = $3.5x10^5$ years), which subsequently decays by both SF and alpha decay to ^{244}Pu ($t_{1/2}$ = 80 Ma). Ultimately launch requirements must meet local environmental standards (e.g. the National Environmental Policy Act).

Planetary protection is critical to the feasibility of the mission. Although traditional planetary protection has been concerned with interplanetary biological and chemical contamination, this instrumentation introduces the possibility of exposing planetary or lunar surfaces to significant neutron fluxes, which could affect existing biology and chemistry on the surface. Issues associated with this must have been addressed to some extent by the DAN instrument included on the Curiosity rover, but flux and fluence levels involved here are significantly higher and must be considered. Although shielding could theoretically reduce these levels, the increased mass of shielding required to protect the entire surface and/or atmosphere (rather than only the rover or lander) is considerable. This is discussed in detail in the feasibility analysis below.

6. Gas extraction and analysis

$^{40}Ar/^{39}Ar$ geochronology requires heating to release argon from the material to be dated. The resultant gas is then cleaned to trap reactive gases and isolate noble gases for mass spectrometric analysis. Below we describe parameters involved in application of these requirements to spaceflight, relying when possible on flight-ready instruments included as part of recent or existing missions.

6.1 Sample heating and gas extraction

Samples must be heated to release Ar gas for analysis. Terrestrially, this is accomplished using a furnace or laser, with desired temperatures of up to 1200°C, depending on the melting temperature and melt viscosity of the sample. These temperatures would prove difficult to reach given recent power capabilities of rover furnaces. For example, the oven in the Sample Analysis at Mars (SAM) instrument suite on the Curiosity rover can heat samples to 950°C, and up to 1100°C using an auxiliary heater (Mahaffy et al., 2012). This can be ameliorated by analyzing smaller grain sizes but also by mixing samples with a lithium borate flux (similar to those used in preparing glass beads for XRF analysis) prior to heating; experiments using this

type of flux have been shown to completely degas basaltic samples at ca. 965°C (Farley et al., 2013). However the use of a flux may affect incremental heating release patterns; this issue should be a major component of future testing, to ensure that argon release patterns are not appreciably affected by use of the flux.

6.2 Gas purification

Terrestrially, noble gases (of which argon is typically the largest component) are purified using solid-state getter material that traps reactive gases. Such systems have been included successfully in the SAM instrument (Mahaffy et al., 2012) and could be used again for a future geochronological mission.

6.3 Mass spectrometry

Isotopic ratio measurements for $^{40}Ar/^{39}Ar$ geochronology are typically made by magnetic sector mass spectrometers. However, magnet masses are prohibitively high for spaceflight and thus recent missions have relied on lower precision quadrupole mass spectrometers, which use energy filters to separate isotopes for detection (Mahaffy et al., 2012).

6.3.1 Abundance sensitivity

Among the most important parameters for our purpose is abundance sensitivity, defined as "the ratio of the maximum ion current recorded at a mass *m* to the ion current arising from the same species recorded at an adjacent mass *(m±1)*" (McNaught and Wilkinson, 1997). Abundance sensitivity is a function of the peak shape and mass resolution of the instrument, and is typically inferior in quadrupole instruments. This is particularly important here, as improved abundance sensitivity allows for the measurement of larger isotopic ratios (e.g. $^{40}Ar/^{39}Ar$), and in turn allows for a lower strength neutron source.

Improving the abundance sensitivity of the quadrupole instrument would significantly affect the required neutron source parameters, as it allows for the measurement of larger isotopic ratios. For reference, the MAP 215-50 magnetic sector mass spectrometer at CalTech

has an abundance sensitivity in the mass 4 range of >2 x 10^{10}, which allows for measurements with 20% precision on ratios of <2 x 10^{9} (Amidon and Farley, 2010). Achieving the somewhat higher precision measurements (e.g. 5-10%) desired here would require somewhat smaller isotopic ratios.

The heritage quadrupole included in SAM has an abundance sensitivity of ca. 10^{5} (Ken Farley, personal communication). However commercially available gas-source quadrupole instruments, including the Hiden HAL series 1000 triple filter quadrupole instrument used in terrestrial $^{40}Ar/^{39}Ar$ work (Schneider et al., 2009) and the Extrel MAX series (UK distributor: Henniker Scientific), evidently reach abundance sensitivities of 10^{7}, representing a potentially significant improvement. Further, plasma-source quadrupole instruments have been modified to yield abundance sensitivities in the mass 40 range of 10^{9} to 10^{10}, by using auxiliary quadrupolar excitation to improve peak shape and tailing characteristics (Konenkov et al., 2001). This technology is apparently available commercially through AB SCIEX but does not yet seem to include gas source instruments, and is not spaceflight ready.

Although significant technological development is required to yield flight-ready quadrupole instruments with high abundance sensitivities, it appears that reaching abundance sensitivity values of 10^{7}, and even 10^{10}, are feasible. These values are used herein to consider the ultimate feasibility of the project and could represent a 100- to 10,000-fold improvement in abundance sensitivity.

6.3.2 Sensitivity and ion detection

The absolute sensitivity of the instrument is of secondary importance, as increasing sample size can ameliorate issues with low sensitivity. Heritage technology available from SAM (adapted from previous missions) includes an ion source and two continuous dynode secondary electron multipliers. This technology could be readily used for this purpose, but instrument stability may be improved by considering the use of high-gain Faraday amplifiers in addition to the electron multipliers. Although $10^{12}\Omega$ resistors have been in use for some

time, recent developments have yielded reliable $10^{13}\Omega$ resistors (Koornneef et al., 2014). Further, a UK company (TIA Systems) has partnered with SUERC to develop $10^{14}\Omega$ resistors. These developments may allow for the replacement of multiplier systems with more stable Faraday detector technology with similar sensitivity characteristics.

6.3.3 Analytical methods

Samples are typically run in series with measurements to determine background and isotopic fractionation in the system. Background values can be determined by following sample analysis procedures without heating a sample. Isotopic fractionation, or discrimination, can be determined by measuring a gas with a known ratio, typically the atmospheric $^{40}Ar/^{36}Ar$. This could be accomplished extraterrestrially by including small fragments of silicate glass that has been heated under the atmosphere and shown to have a specific (likely near-atmospheric) ratio. These glass fragments would be produced on Earth and included in the launch package so that they can be occasionally heated to determine the mass discrimination of the system during analysis.

7. Feasibility Analysis

Many complex parameters, as discussed above, are involved in the deployment of an extraterrestrial in situ $^{40}Ar/^{39}Ar$ geochronology device using a passive neutron source and quadrupole mass spectrometer. These parameters are discussed in combination here to identify potential opportunities for the future application of this method. Issues considered include mass, power, data quality, analysis time, and cost.

7.1 Requirements

System requirements are twofold:

1. To create sufficient ^{39}Ar during irradiation in a reasonable length of time for measurement of precise (e.g. 5-10%) $^{40}Ar/^{39}Ar$ ratios on rocks as old as 4.6 Ga.

2. To release argon from rock samples by heating and measure argon isotopes (masses 40, 39, 38, 37 and 36) on released gas.

7.2 Limitations

7.2.1 Mass

Mass is an important consideration for spaceflight applications due to high launch costs. For planetary applications of this technology, mass then is among the most important considerations. For use in an Earth-side containment facility, however, mass is significantly less constrained.

Among the benefits of relying on ^{252}Cf as a passive neutron source is the small mass (43 mg) required to obtain a source strength of 10^{11} n/s (Table 1). However, as discussed below, ^{252}Cf is an extremely expensive material, and 43 mg is approximately the amount produced annually in the US. We thus consider the use of neutron multiplier ^{235}U, which would add significant mass to instrument package (Figure 7) but may allow for less ^{252}Cf to be used, and/or balance out the effects of ^{252}Cf decay over the life of the mission. This may also allow for a “switchable” source, which would act to reduce total fluence seen by instruments (and humans prior to launch). The use of a multiplier could theoretically allow for a rover system to temporarily leave the source and shielding behind for the period of irradiation, and return to collect them when it has switched to lower flux levels. This approach could significantly limit the required shielding, as discussed below. However, the addition of a ^{235}U multiplier would add considerable mass, requiring ca. 10 kg for a multiplication factor of 2, and nearly 50 kg for a factor of 10. Neutron multipliers could more readily be used as part of a neutron source to be built in a containment facility for returned samples.

Another major component of the mass budget is neutron shielding. In particular, shielding must protect other mission instruments, potentially the planetary surface, and humans during preparation and launch. Shield materials act to absorb and/or moderate neutrons, and in the process decrease the total neutron energy (Figure 5). Potential shield materials and composite shields have been assessed for their shielding efficiency with respect

to mass and thickness (Figure 8). Neutron moderators investigated here are Premadex, HDPE, Paraffin, and B4C. Neutron absorbers are Premadex (due to its ^{6}Li content), B_4C, Cd, and Gd. Note that neutron absorbers more effectively absorb thermal neutrons and thus can act to increase the relative fast: thermal neutron ratio even while decreasing the total neutron flux. Composite shields containing materials with both moderating and absorbing properties are likely to be the most effective, as moderating material acts to decrease the energy of fast neutrons; the resultant thermal (or epithermal) neutrons can then be more effectively stopped by absorbing material.

Importantly, results in Figure 8 do not incorporate the geometric effect, which relies purely on distance from the source and does not require shielding material. This effect is quite considerable (e.g. decrease in flux of 10^4 over 1 meter of space. Implementing this effect would require carefully locating the source within the instrument package so that the most sensitive instruments are at the greatest distance from the source; it may also be feasible to mount the source on an arm or otherwise distance it from the instrument package. Although some shield material will no doubt be useful in moderating neutron energies, employing this geometric effect will be integral to the mass-efficient application of this technology to planetary surfaces. The mass of shielding may also be reduced geometrically, depending on the planetary protection concerns, if irradiation of the planetary surface and atmosphere is acceptable.

Although much of the technology required for $^{40}Ar/^{39}Ar$ analyses can be realized using equipment from previous missions, there exists room for improvement in mass spectrometry. The quadrupole instruments described in the above section on mass spectrometry would allow for at least 100-fold improvement in abundance sensitivity, which would decrease the required ^{39}Ar production, thus the required neutron fluence. This affects mass by limiting the required source strength and thus multiplier material and shielding required to produce measureable $^{40}Ar/^{39}Ar$ values over reasonable irradiation durations. However, these improved quadrupole instruments also have higher mass. For example, the Hiden HAL series 1000 triple filter instrument described above has a quadrupole filter of ca.

10.5 kg and RF generator of ca. 15 kg, while the Extrel MAX series instrument weighs ca. 40 kg in total. It should be noted that these earth-based instruments have not likely been constructed with the intention of limiting the mass of the instrument. In contrast, the entire SAM instrument suite on Curiosity, including a quadrupole, gas chromatograph, tunable laser spectrometer, and sample handling capabilities, also weighs 40 kg. However, it may be more mass- and cost-efficient to utilize these improved spectrometers, or lower mass derivations of them, rather than rely on increased ^{252}Cf and shielding, to achieve the same measurement precision.

7.2.2 Power

One benefit of using ^{252}Cf is that as a spontaneous fission neutron source, it requires no power. Minimal power may be required if a 'complex cylindrical geometry' with moveable or rotatable pins of multiplier material is utilized. Further power requirements include sample drilling and handling, sample heating during gas extraction, and mass spectrometry. The first two of these should not vary considerably from requirements in SAM, as heating samples in contact with a lithium borate flux will act to effectively decrease the melting temperature of the sample to temperatures accessible by the furnace on SAM (Farley et al., 2013; Mahaffy et al., 2012).

The implementation of a quadrupole mass spectrometer with improved abundance sensitivity would likely require more power than the QMS on SAM due in part to the higher power requirements for generating the RF field. For example, the Hiden HAL series 1000 triple filter instrument typically draws ca. 260 W, with an absolute maximum of ca. 650 W. This can be compared with the available power from the MMRTG on Curiosity, which has a maximum of 110W, although 42 amp-hour batteries do allow for higher power draws.

It should also be considered that heat generated within the neutron source could be used to partially power the mission, in addition to the MMRTG units used on recent missions.

7.2.3 Data quality

The primary motivation for developing this technology is to obtain *accurate* age constraints for extraterrestrial samples. The critical feature of the $^{40}Ar/^{39}Ar$ method that allows for this is the capacity for incremental heating of samples to interrogate thermal histories. The quality of the age spectra obtained from step heating experiments (ie: the reproducibility of ages between sequential heating steps) will ultimately control the precision of obtained ages; this will be linked directly to sample selection and quality. Variability between steps may in fact indicate complex thermal histories that would not be identified by other means (e.g. sample in Figure 1).

The precision of ages for each incremental heating analysis is also an important factor and relies largely on the measurement precision of the $^{40}Ar/^{39}Ar$ ratio. Given that extraterrestrial samples will be sufficiently old that measureable quantities of ^{40}Ar have ingrown from ^{40}K (even in low K samples), the limiting factor here will be the production of ^{39}Ar from ^{39}K by neutron irradiation. The amount of ^{39}Ar produced, along with the ability to measure small ^{39}Ar beams next to large ^{40}Ar beams (abundance sensitivity) will thus control the attainable precision of each analysis. The acceptable level of precision will likely be significantly lower than typically achieved terrestrially, which will allow for the measurement of smaller ^{39}Ar beams.

7.2.4 Analysis time

The time required for analysis may be a factor if this technology is implemented as one component of a larger mission. Although neutron irradiation durations will be long, the process is largely passive and thus does not require the exclusive use mission capabilities. A multipurpose rover, for example, could be driving and/or performing other tasks during the months-long irradiation period. Sample drilling and preparation would require the use of drills and other automated sample handling components. Sample heating, particularly at higher temperature steps, would likely use much of an instrument package's power requirements, and thus during this time (typically tens of minutes) other activities would cease. Power requirements of the mass spectrometer would similarly require exclusive use of a typical

power source. Terrestrially, gas extraction, purification, and measurement are typically completed within 20-30 minutes per analysis. Given the need for background and discrimination measurements, as well as incremental heating of samples, each sample may require ca. 2 days of analytical time.

Typically samples are run in series with background and air analyses. The frequency with which these are measured will have some effect on the achievable precision and could require significant analytical time.

7.2.5 Cost

The major cost for this mission involves the procurement of ^{252}Cf. Although only 43 mg is required to produce an acceptable neutron flux, this material is produced in very small quantities in only one known location. The High Flux Isotope Reactor (HFIR) at Oak Ridge National Laboratory (ORNL) typically produces only ca. 40 mg of ^{252}Cf per year, which sells at a cost of ca. £400,000/mg. The high cost is due to the large number of high energy neutrons (>2000) required to produce each atom of ^{252}Cf. The quantity required for this mission (43 mg for a source strength of 10^{11} n/s without multiplication) thus would utilize much of the available material. Further, the short $t_{1/2}$ would require that the material be made as close to launch as possible, and that an initially higher quantity be included in the mission to account for decay during transit.

The second major cost for a mission involving this technology would be costs associated with launching the instrument package. For example, recent launches to Mars have cost ca. $10,000/kg. Potentially high mass components include multiplier and shield material and a high abundance sensitivity mass spectrometer. The requirement for these materials is linked in that an improved mass spectrometer would allow for the measurement of smaller quantities of ^{39}Ar; thus source strength could be decreased, limiting the required amounts of costly ^{252}Cf and high mass multiplier and shielding material. Identifying the most efficient

balance between these factors will play a key role in the potential for future success of the project.

7.3 Calculations toward potential solutions

7.3.1 Preferred solution

The preferred solution herein involves the technological development of a quadrupole (or other light) mass spectrometer for spaceflight with improved abundance sensitivity. Development could focus on technologies such as those in the Hiden or Extrel instruments, which have abundance sensitivities of ca. $1x10^7$. Technological development should in part focus on mass reduction to make the instrument more amenable to spaceflight applications.

Assuming an improved abundance sensitivity of the mass analyzer to $1x10^7$, it should be possible to measure with reasonable precision (5-10%) $^{40}Ar/^{39}Ar$ ratios of ca. $5x10^5$ to obtain ^{39}Ar signals of ca. 50x the peak tail value. Peak tail effects can be quantitatively analyzed prior to launch by measuring similarly under-irradiated samples. Calculations presented in Figure 2 indicate this is achievable by a 100 day irradiation (an arbitrary but reasonable duration) in a neutron flux of $6.73x10^8$ n/cm^{2}s. Given a source at a distance of 1 cm from the sample, this would require a source strength of $8.46x10^9$ n/s, which in turn requires only 1.22 mg of ^{252}Cf (Table 1) (at a cost of ca. £1.5M). The time that will pass between ^{252}Cf manufacture and irradiation (depending on logistics and largely on flight time to destination) will require additional ^{252}Cf to account for its relatively short $t_{1/2}$ of 2.645 a.

Shielding a source this size could be effectively accomplished with a reasonable mass of shielding. As shown in Figure 5a, a 30 cm shield of HDPE significantly decreases the neutron energy by scattering. Data presented in Figure 8 show that ca. 3% of neutrons remain at the surface of a 35 cm HDPE or Premadex® shield; this flux could be further reduced by introducing a thin film of neutron absorbing material around the neutron moderator (Figure 8b). The 30 cm HDPE shield alone would reduce the flux at the shield surface to ca. $6.75x10^6$ n/cm^{2}s, already under the apparent tolerance of 10^7 n/cm^{2}s for the most sensitive components (CCD) included in the Curiosity rover mission. Assuming that shielding is only required for

mission instruments (and not the planetary surface), only a small fraction of a spherical shield would be required, and this fraction would decrease with increased distance between the neutron source and other instruments. Given 1 meter distance between the source and sensitive mission components, geometry reduces the fraction of shield required to cover a 1 meter high and wide instrument package to ca. 6% of the total sphere. Given a material density of 0.97 g/cm^3 and the above distances, a 35 cm shield could have a mass of <11 kg.

Further, this shield efficiency does not account for geometric effects, which reduce the flux by the inverse square of the radius. Applied over the entire 1 meter distance between the sample chamber and other instruments, this effect would act to further reduce the flux by a factor of ca. 0.000816 to ca. 5.5x10^3 n/cm^{2}s, several orders of magnitude lower than the tolerances of the sensitive CCD components on Curiosity.

The total mass of the instrument package in this case is largely reliant on the mass of the quadrupole instrument and shielding. As noted above, shielding amounts may be limited by the use of a thinner shield, and potentially also by implementing only a partial shield to cover the other instruments. Indeed, given a similar sample chamber flux (at 1 cm from the source) of 2.25x10^8 n/cm^{2}s and only accounting for the geometric effect, the flux at 35 cm reaches 1.8x10^5 n/cm^{2}s. The use of distance rather than high mass shielding material is more likely to produce an acceptably low neutron flux in an instrument package with an acceptably low mass. The quadrupole instrument mass may also be reduced through technological development and substitution of certain components for those with lower mass.

7.3.2 Alternate solution

An alternate approach would use existing spaceflight-ready quadrupole technology from SAM and instead focus on increasing the neutron flux. This can be accomplished by a combination of the procurement of additional ^{252}Cf and the use of ^{235}U as a neutron multiplier. Reducing the neutron flux to acceptable levels in this situation would require more shield material for two reasons: first, a higher flux requires more shielding to reach acceptable neutron flux levels for other system components, and second, this requires a larger source

volume and thus larger volume of shield material to cover. For example, the abundance sensitivity of the heritage instrument on SAM is ca. 10^5. Reasonably precise $^{40}Ar/^{39}Ar$ ratios of ca. $5x10^3$ should be measureable, again with signals of ca. 50x the peak tails. Achieving this ratio within a similar irradiation duration of 100 days requires a neutron flux of $6.73x10^{10}$, two orders of magnitude higher than the previous case. Shielding a larger signal would subsequently require additional neutron shielding material and/or distance between the source and other neutron sensitive components.

8. Conclusions

The challenges and costs involved in such an ambitious mission are clearly substantial—from the procurement of ^{252}Cf, to the launch of tens of kilograms of instruments, to the time requirements for analyses. However the combination of technology described herein is feasible and has the potential to *accurately and reliably* answer a major remaining question in many extraterrestrial environments—"how old is it?" By selectively deploying this instrument package to any number of planetary and/or asteroidal surfaces, we can begin to decipher the history of these bodies and their places in the solar system.

We have shown that numerous related and often competing factors would be involved in the development of this technology. One potential solution, involving an improved mass spectrometer will enhanced abundance sensitivity, perhaps provides the most feasible approach by limited the required neutron source strength and thus required shielding. Further technological developments that improve abundance sensitivity in lower mass quadrupole instruments would allow for the extraterrestrial application of not only $^{40}Ar/^{39}Ar$ geochronology but also other scientific functions.

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Figure Captions

Figure 1. Age spectrum for pyroxene from meterorite Allan Hills 84001, modified with permission from Cassata et al. (2010), and provided as an example of the effects of thermal events on apparent ages. Approximate formation, impact, and apparent K-Ar (total gas) ages are shown as gray bars. Note the difference between the apparent impact and formation ages, as well as the approximate age that would have been determined by application of the K-Ar method to this sample. This illustrates the potential for the K-Ar method to yield biased ages, with no means of identifying that bias. Many extraterrestrial samples yield similarly complex age spectra.

Figure 2. Required source flux and irradiation duration to reach various $^{40}Ar/^{39}Ar$ ratios for a 4 Ga sample. Each line represents a different $^{40}Ar/^{39}Ar$ ratio; movement along that line shows the range of source fluxes and irradiation durations required to attain that ratio. The fast neutron flux ($2.5x10^{13}$ n/cm^2s) in the CLICIT facility of the Oregon State University TRIGA reactor is shown for reference, as is a maximum "reasonable" but arbitrary irradiation duration of 100 days. For example, a $^{40}Ar/^{39}Ar$ ratio of 10^5:1 can be reached with a ca. $3.3x10^9$ n/cm^2s neutron flux over ca. 100 days.

Figure 3. Neutron energy spectra for ^{252}Cf and ^{235}U, using parameters corresponding to their respective Watt fission spectrums, along with the neutron capture cross-section for the $^{39}K(n,p)^{39}Ar$ reaction from ENDF. Note that the ^{252}Cf spectrum is slightly higher energy than the ^{235}U spectrum, and thus more favorable for the $^{39}K(n,p)^{39}Ar$ reaction. Reproduced with permission from Li et al. (2011).

Figure 4. Neutron source geometries explored and modeled herein. **(a)** Cross-section of concentric spherical source, with point source of ^{252}Cf surrounded by spherical sample chamber (void) and reflector material. **(b)** Cross-section of similar concentric spherical source, with the addition of ^{235}U neutron booster or multiplier material. **(c)** Overhead and side

709views of cylindrical source, with central ^{252}Cf source surrounded by sample chamber (void)
710and reflector material. ^{235}U neutron multiplier material is located in rotatable or removable
711pins to allow for control over source neutron flux.
712
713**Figure 5.** Results from MCNP modeling of neutron flux in simple spherical source (e.g.
714Figure 4a) with a 30 cm thick HDPE shield. Modeled neutron energy spectrum in sample
715chamber (black) and those neutrons that escape from the shield (gray). Energies of many
716neutrons exiting the shield are lower due to scattering in the low-Z shield material. The
717neutron flux in the Y-axis is normalized to lethargy, which accounts for the scattering
718efficiency of the incident material.
719
720**Figure 6.** Results from MCNP modeling of spherical source geometry as in Figure 4b.
721Efficiency of ^{9}Be multiplier with a range of thicknesses and masses, representing the
722additional neutrons created by the multiplier. Model completed using Premadex® as reflector
723material; reflector thickness did not appreciably affect results.
724
725**Figure 7.** Results from MCNP modeling of spherical source geometry as in Figure 4b.
726Multiplication efficiencies of 90% enriched $^{235}UO_2$ and 100% enriched other transuranic
727isotopes, are shown against thickness and mass of booster material. Models completed using
728Premadex® as reflector material; reflector thickness did not appreciably affect results. Similar
729results are found with variable sample void radii.
730
731**Figure 8:** Results from MCNP modeling showing the efficiencies (provided as a fraction of
732remaining neutrons) of various shield materials, based on a simple concentric spherical
733geometry (Figure 4a). Note that efficiencies are based on collisions within the material and do
734not account for geometric effects. Neutrons of all energies are included in calculations. **(a)**
735Shield efficiencies for high-density polyethylene (HDPE), Premadex®, B_4C, Cd, Gd, and
736paraffin. See Figure 5 for neutron energy spectrum for HDPE shield. **(b)** Shield efficiencies

for composite shields of Premadex® combined with a variety of materials. **(1)** 20 cm of Premadex® surrounded by 14 cm of the other material. **(2)** B_4C alternates with Premadex® every 2 cm in the shield. **(3)** Premadex® with two layers of B_4C, of 8 cm and 6 cm thickness.

28

Table 1. Passive neutron sources decaying by spontaneous fission. These are more efficient than reactions on Be (e.g. Li et al. Table 1). ^{252}Cf is selected here due to its availability, high neutron flux per unit mass, and low heat output. Heat output is provided in watts produced by the mass required to achieve source strengths of 10^{11} n/s.

Source	**Mass required for 10^{11} n/s**	**n/s/mg**	**$t_{1/2}$**	**SF branching ratio (%)**	**Heat Output (Watts/10^{11}n/s source)**
^{252}Cf	43 mg	$2.3x10^{9}$	2.645 years	3.82	1.43
^{250}Cf	9.5 g	$1.1\ x10^{7}$	13.08 years	0.08	31
^{248}Cm	2.14 kg	$4.7\ x10^{4}$	$3.5x10^{5}$ years	8.26	1.04
^{246}Cm	9.8 kg	$1.0\ x10^{4}$	$4.7x10^{3}$ years	0.03	90
^{244}Cm	9.8 kg	$1.0\ x10^{4}$	18 years	$1.3x10^{-4}$	$2.4x10^{4}$
^{253}Es	274 g	$3.6\ x10^{5}$	20 days	$8.7x10^{-6}$	$2.1x10^{5}$
^{254}Fm	0.2 mg	$3.4\ x10^{11}$	3.24 hours	0.06	33

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