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In Situ Radiometric Dating on Mars: Investigation of the Feasibility of K-Ar Dating
using Flight-Type Mass and X-ray spectrometers

D.L. Talboys^{a*}, S. Barber^b, J.C. Bridges^a, S.P. Kelley^c, D. Pullan^a, A.B Verchovsky^b,
5 G. Butcher^a, A. Fazel^c, G.W. Fraser^a, C.T. Pillinger^b, M.R. Sims^a, I.P. Wright^b

*^aDepartment of Physics and Astronomy, University of Leicester, University Road,
Leicester LE1 7RH, UK*

10 *^bPlanetary and Space Sciences Research Institute, The Open University, Walton Hall,
Milton Keynes MK7 6AA, UK*

*^cDepartment of Earth Sciences, The Open University, Walton Hall, Milton Keynes
MK7 6AA, UK*

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Abstract

The absolute chronology of Mars is poorly known and as a consequence a key science
aim is to perform accurate radiometric dating of martian geological materials. The
scientific benefits of in situ radiometric dating are significant and arguably of most
20 importance is the calibration of the martian cratering rate, similar to what has been
achieved for the Moon, to reduce the large uncertainties on absolute boundary ages of
martian epochs. The Beagle 2 Mars lander was capable of performing radiometric
date measurements of rocks using the analyses from two instruments in its payload: (i)

* Corresponding author. Tel. +44 (0)116 252 5084.

E-mail address: dlt3@star.le.ac.uk (D.L. Talboys)

the X-ray Spectrometer (XRS) and (ii) the Gas Analysis Package (GAP). We have
25 investigated the feasibility of in situ radiometric dating using the K-Ar technique
employing flight-like versions of the Beagle 2 instrumentation. The K-Ar ages of six
terrestrial basalts were measured and compared to the ‘control’ Ar-Ar radiometric
ages in the range 171 – 1141 Ma. The K content of each basalt was measured by the
flight spare XRS and the ^{40}Ar content using a laboratory analogue of the GAP. The K-
30 Ar ages of five basalts broadly agreed with their corresponding Ar-Ar ages. For the
final basalt, the ^{40}Ar content was below the detection limit and so an age could not be
derived. The precision of the K-Ar ages was ~30% on average. The conclusions from
this study are that careful attention must be paid to improving the analytical
performance of the instruments, in particular the accuracy and detection limits. The
35 accuracy of the K and Ar measurements are the biggest source of uncertainty in the
derived K-Ar age. Having investigated the technique using flight-type planetary
instrumentation, we conclude that some of the principle challenges of conducting
accurate in situ radiometric dating on Mars using instruments of these types include
determining the sample mass, ensuring all the argon is liberated from the sample
40 given the maximum achievable temperature of the mass spectrometer ovens, and
argon loss and non-radiogenic argon in the samples analysed.

Keywords: Mars Chronology; Planetary Instrumentation; Radiometric Dating; X-ray
Fluorescence Spectrometry; Mass Spectrometry.

45

1. Introduction

The absolute chronology for Mars is poorly known and, as a consequence, there are significant scientific returns achievable from in situ radiometric dating on Mars by robotic landers (for a review see Doran et al., 2004). An important science aim for in situ dating would be to calibrate the martian cratering rate (Plescia and Swindle, 2007). For the Moon, the crater density is calibrated in absolute terms by dating returned samples from the Apollo and Luna missions (Stöffler and Ryder, 2001). However, since there have been no sample return missions for Mars, its cratering rate can only be inferred from the Moon (Neukum et al., 2001). As a consequence of this and discrepancies with the crater density reported by various authors, there are large uncertainties associated with the absolute chronology of martian epochs (Hartmann and Neukum, 2001). Since the relative stratigraphy and chronology is already established for much of Mars (Tanaka, 1986; Scott and Tanaka, 1986; Greeley and Guest, 1987; Tanaka and Scott, 1987; Tanaka et al., 1992; Hartmann and Neukum, 2001), the absolute chronology of martian history could be constrained through the determination of the radiometric ages of samples at certain key sites. An ideal target to achieve this would be igneous rocks located at key sites where the relative stratigraphy (and hence chronology) and geological context is well defined. Other suitable targets for radiometric dating include: young volcanic lava flows, widespread ash deposits (e.g., in the polar layered deposits) and fluvial and lacustrine events using K-rich salts in sediments (Doran et al., 2004).

A radiometric dating scheme that could be usefully applied in situ on Mars is K-Ar dating. This is based on the decay of the radioactive isotope of potassium, ^{40}K , into ^{40}Ar , with a half life of 1.25 billion years, and uses the absolute abundances of these isotopes in the rock to derive the age. Given the 1.25 billion year half-life of ^{40}K , the

useful period for K-Ar dating is for rocks older than several tens of thousands of years in age. Although potassium is a major constituent of many rock-forming minerals, its only radioactive isotope, ^{40}K , has a relatively small naturally occurring isotopic abundance of 0.012%. The major branch for decay into the radiogenic isotope ^{40}Ar is through capture of an electron, usually from the K shell, which combines with a proton to form a neutron. The principle mode of ^{40}K decay, however, is to ^{40}Ca through the emission of a beta particle from its nucleus and the conversion of a neutron into a proton. The abundance of ^{40}Ca is not measured relative to ^{40}K for radiometric dating because of the large amounts of non-radiogenic ^{40}Ca that is typically present in rocks. In contrast, ^{40}Ar , the most abundant isotope of Ar, as a noble gas is not a major constituent of rocks. When a rock forms (while in a molten state), it will not retain ^{40}Ar until it cools to a sufficient temperature; it is at this time the potassium-argon clock is 'set' and the ^{40}Ar from ^{40}K decay can accumulate. ^{40}Ar is only liberated if the mineral is melted, recrystallised or heated to a temperature that will allow the ^{40}Ar to diffuse through the mineral lattice. The K-Ar dating technique relies on accurately determining the amount of radiogenic ^{40}Ar that has decayed from ^{40}K , and accounting for both non-radiogenic argon (of atmospheric and/or magmatic origin) and mechanisms of argon loss which would bias the age determination.

Measurement of the potassium content of the rock can be performed using various geochemical analytical methods, although we will focus on the technique of X-ray fluorescence spectroscopy, as discussed in section 2.2. The argon content of the rock is typically measured using the technique of mass spectrometry (discussed in section 2.3) where the sample is incrementally heated to release the trapped argon from various mineral domains within the rock.

Ar-Ar dating has superseded K-Ar dating as a modern geochronological technique. In this scheme, the rock is irradiated with fast neutrons which converts atoms of ^{39}K in the rock (present, like ^{40}K , to a known isotopic abundance) into ^{39}Ar via a n,p (neutron capture, proton emission) reaction. The ^{39}Ar is used to infer the abundance of ^{40}K since their relative isotopic abundances are known. Thus the relative amounts of ^{40}K and ^{40}Ar can be measured simultaneously using a mass spectrometer, which means the accuracy of the technique is better than the K-Ar scheme, where the absolute abundances of K and Ar are determined using two analytical techniques. A major advantage of Ar-Ar dating is that the profile of the cumulative argon isotope loss during step heating is an indicator of whether radiogenic argon loss or non-radiogenic argon gain has occurred. However, because of the need to irradiate the rock sample with high fluences of neutrons before analysis, Ar-Ar dating is a technique that would be difficult to implement using robotic instrumentation on Mars.

Beagle 2, the exobiological lander for ESA's Mars Express orbiter (Schmidt, 2003), is the only Mars mission launched to date with the explicit aim to perform in situ K-Ar radiometric dating of rocks (Wright et al., 2003). Unfortunately, the Beagle 2 lander failed to communicate during its first expected radio contact on 25th December 2003 and hence this science objective was not fulfilled. In situ radiometric dating would have been performed using two instruments in the lander's payload with the potassium content measured by the X-ray Spectrometer (XRS), designed to perform geochemical analyses of rocks and soils, and the argon isotope content measured by the Gas Analysis Package (GAP), a mass spectrometer, capable of analysing the isotopic composition of atmosphere, rock or soil samples. The GAP would also have performed an additional radiometric age measurement, the Cosmic Ray Exposure

(CRE) age, based on the analysis of cosmogenic nuclides ^{21}Ne and argon ^{36}Ar (although not ^3He since GAP is unable to detect this isotope) that are produced by
125 cosmic ray nuclear interactions with nuclei in rocks and accumulate over time (Doran et al., 2004; Eugster, 2003). Isidis Planitia, the planned landing site for Beagle 2, had extensive volcanism during the Hesperian into the late Amazonian epochs and so any in situ dating could have potentially constrained the absolute chronology of these epochs (Bridges et al., 2003).

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In addition to the GAP, which was essentially an on-board laboratory, the deployable elements of the Beagle 2 payload were designed to provide geological context, which is essential to reliably interpret the radiometric ages of rocks. This payload comprised a package of imaging devices, contact analytical instruments and sampling tools
135 called the Position Adjustable Workbench (PAW), situated on the end of a robotic arm. The Stereo Camera System (Griffiths et al., 2005) consisted of two cameras, positioned on opposite sides of the PAW, which could deliver panoramic images of the landing area using multispectral filters. The Microscope could perform close up imaging of rocks and soils (with its own illumination from LEDs) to provide
140 information on surface texture and probe for microstructures of possible biological origin (Thomas et al., 2004). The Mössbauer Spectrometer (Klingelhöfer et al., 2003) had the primary aim identifying the relative abundances of iron-bearing minerals in rocks. The payload also included two subsurface sampling tools (Richter et al., 2002). The first tool was the Rock Corer-Grinder which could remove the weathered and
145 dust covered surface layers of rock to expose the 'fresh' interior and also sample cores or rock chippings (depending on the material) for delivery to the GAP. The second

tool was the Planetary Underground Tool which could sample the subsurface regolith by penetrating 1.5 m into the martian surface.

150 K-Ar radiometric dating of rocks was a consequence of the general operational strategy for Beagle 2 called the 'rock analysis cycle' (Pullan et al., 2004). After an initial survey using the Stereo Camera System, a target rock would be chosen. This rock would be intensively imaged by the cameras from various angles utilising the geological and stereoscopic filters. The Microscope, Mössbauer Spectrometers and
155 XRS would then perform measurements on the weathered surface of the rock. The Rock-Corer Grinder would then drill through the surface and sample an interior portion of the rock and deliver ~100 mg of chippings to the inlet port of the GAP for analysis of isotopic composition, including the argon isotope content. The prepared surface would then be analysed using the XRS to determine the geochemical
160 composition, including the potassium content. In addition, further measurements on the prepared surface would also be made using the Microscope and Mössbauer Spectrometer in order to compare the weathered surface of the rock to its interior.

In terms of future missions to Mars, the Mars Science Laboratory (MSL) will carry a
165 payload capable of K-Ar dating. The Sample Analysis at Mars (SAM) instrument, which comprises a Gas Chromatograph Mass Spectrometer (GCMS) and pyrolysis oven, will analyse the noble (including Ar) gas content of martian rocks whereas the K content will be measured by instruments which exploit the geochemical analysis techniques of X-ray spectroscopy and laser induced breakdown spectroscopy (Park et
170 al., 2009). Studies of the radiometric dating technique when applied to robotic payloads show promise, for example Swindle (2001) found that the age of martian

meteorites can be determined using K-Ar dating to an accuracy of ~20%. As a consequence, there are many instruments at the proposal or early development stages that use various techniques, including Rb-Sr, Cosmic Ray Exposure (CRE) Age and
175 Optically Stimulated Luminescence / Thermoluminescence dating, (Anderson et al., 2006; Kalchgruber et al., 2007). One system of note has been developed specifically for K-Ar dating, called the Argon Geochronology Experiment (AGE), is also capable of measuring the CRE age (Swindle et al., 2003). The potassium abundance is measured using the Laser-Induced Breakdown Spectroscopy (LIBS) technique and
180 Ar, He and Ne isotope content is measured using a miniature Quadrupole Mass Spectrometry Array (QMSA). The samples are delivered to one of 12 sample crucibles each of which is transferred for analysis by LIBS and QMSA. Each crucible is an oven in which the samples are heated to temperatures of 1500°C to liberate the noble gases. The package has relatively modest resource requirements with a mass of
185 5.7 kg, volume of 30×28×16 cm and power from 10 W up to 180 W for the short periods when the ovens are in use.

Although it is clear that there are major scientific returns from in situ radiometric dating, the technique when applied by robotic payloads needs to be characterised.
190 Indeed, the Committee on Planetary and Lunar Exploration (COMPLEX, 2003) recommended: "... that studies of the feasibility of in situ determination of rock ages, by robotic spacecraft, be pursued". As Beagle 2 would have performed the first measurement of this kind on the surface of Mars, and that this measurement may well be attempted in the future, we performed a preliminary assessment of the capabilities
195 of in situ K-Ar dating using laboratory analogue versions of the GAP and XRS. We

also discuss the difficulties and operational constraints inherent to practically achieve this measurement on Mars using robotic payloads.

For this study we employed laboratory analogues to the GAP and XRS that were
200 sufficiently similar to the flight versions in operation and analytical performance, as
discussed in detail in sections 2.2 and 2.3, for the purposes of this work. The
individual potassium and argon isotope measurements were performed on martian
analogue rocks samples (discussed in detail in section 2.1), specifically six fine-
grained basalt slabs, selected because they are a rock petrology prevalent on Mars and
205 had a broad range of ages similar to martian meteorites. The K-Ar ages derived from
these measurements were compared to the more reliable ‘benchmark’ Ar-Ar ages.

2. Experimental technique

2.1 Rock samples

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Although it is not possible to find direct analogues for martian surface basalt flows on
Earth, the most appropriate terrestrial rocks are basalts in large igneous provinces
such as Deccan Traps in India, or the Ontong Java Plateau in the Pacific ocean. Such
215 basalts form part of large volcanic fields driven by the impact of a mantle plume,
although on Earth these are known to migrate and are related to the break-up of
continental landmasses. In fact, the most appropriate example are basalts from a
province formed during the early Jurassic period, which had a peak eruption time
around 183 million years ago, similar to the known ages of martian shergottite
220 meteorites, which are in the range 170-474 Ma (Nyquist et al., 2001). The similar age

of these rocks means we are able to demonstrate the capabilities of the laboratory analogues of the XRS and GAP on rocks with very similar concentrations of radiogenic argon and potassium. Also included is an older sample, around 1140 Ma, with a similar age to nakhlites (Nyquist et al., 2001). In addition to their age and
225 composition, the fact that these rocks have been at low temperatures (close to the pole), although not necessarily frozen for most of their history, is an additional criterion to qualify them as martian analogues.

The samples are from the Dronning Maud Land LIP which forms part of the Ferrar
230 (Australia) – Karoo (South Africa) – DML (Antarctica) Large Igneous Province which erupted around 183 million years ago close to the time of initial break-up of the Gondwana super-continent. They are tholeitic basalts, similar in composition to modern day examples such as Hawaii. They are dominated by minerals such as plagioclase feldspar, olivine and pyroxene with grain sizes of the order of a
235 millimetre, but the main potassium bearing phases are the feldspar and groundmass of glass and fine grained minerals between the larger grains with grainsizes an order of magnitude smaller, around 0.1 mm. The main challenge in dating such terrestrial rocks is alteration by later fluids which leads to the growth of clay minerals and breakdown of some of the original minerals, particularly olivine. Several analytical
240 techniques have been developed in order to circumvent the problem of alteration and obtain eruption ages, most notably Ar-Ar dating, using a stepped heating technique. This was the technique employed to obtain the ages of the rocks used during this experiment and against which the K-Ar ages were compared.

245 For detailed explanation of the Ar-Ar dating technique and stepped heating, the reader
is referred to McDougall and Harrison (1999). The full data tables and description of
the samples can be found in Fazel (2007). In brief, samples of basalt were wrapped in
aluminium foil and irradiated at the McMaster reactor, Canada. The GA1550 biotite
age standard, with an age of 98.79 ± 0.96 Ma (Renne et al., 1998), was used to
250 monitor the fast-neutron flux. The analysis consisted of stepped heating of 1-2 mg
fragments of basalt using a focused CW Nd-YAG infra-red laser with an external
shutter. The released gases were cleaned by Zr-Al getters and the resulting argon gas
admitted into a MAP 215-50 noble gas mass spectrometer. Mass peaks from 35 to 41
were scanned ten times over ten minutes in peak hopping mode and the concentrations
255 were extrapolated back to the inlet time. Analyses were corrected for blanks, ^{37}Ar
decay and neutron-induced interference reactions. All errors on plateau ages are
quoted at the 2-sigma level.

2.2 Potassium Measurement: X-ray Spectrometer

260 The Beagle 2 XRS was designed primarily to perform an analysis of the major and
trace element composition of rocks and soils. The XRS has several similarities with
previous X-ray Spectrometers deployed on Mars. It utilises the same radioisotope
sources as the X-ray Fluorescence Spectrometer (XRFS) on the Viking landers (Clark
265 et al., 1977) and the fluorescent X-rays are detected by the same solid state detector as
that employed for the Pathfinder APXS (Rieder et al., 1997). Primary excitation is
provided by two ^{55}Fe (105.6 MBq) sources (emitting Mn K X-rays of 5.90 and 6.49
keV) and two ^{109}Cd (8.77 MBq) sources (emitting Ag K X-rays of 22.16 and 24.94
keV). The fluorescent X-rays are detected by an AMPTEK Si PiN diode which has a

270 thickness of 300 μm and area of 7 mm^2 . Detectable elements range from Na ($Z=11$) to
Nb ($Z=41$). As part of the instrument development program, a flight spare instrument
was reserved for characterising the instrument's analytical and operational
performance in the laboratory. The Full Width Half Maximum (FWHM) resolution of
the flight spare XRS employed for this study was ~ 390 eV at Mn K_{α} (5.9 keV).

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The XRS is divided into two parts: the detector head assembly (DHA, shown in Fig.
1, and the Back End Electronics (BEE). For the flight model XRS in the payload of
Beagle 2, the DHA was part of the Beagle 2 PAW package whereas the BEE was
situated in the main body of the lander. The BEE consists of a single electronics board
280 (120 \times 80 \times 15 mm) of mass 98 g. The DHA consists of an aluminium cover
approximately cylindrical in shape of diameter 47 mm, height 47 mm and mass 58 g,
which houses electronic circuit boards and the Si-PiN diode. A carbon fibre reinforced
plastic (CFRP) structure on the front of the Al cover houses the four radioisotope
sources. Two ^{55}Fe sources are mounted in the front of the CFRP structure and two
285 ^{109}Cd sources are mounted in the rear at 90° positions to the ^{55}Fe sources. Uniquely
for an X-ray spectrometer, the sample is excited by two types of sources
simultaneously as opposed to sequential source excitation used in some terrestrial X-
ray Spectrometers (Potts et al., 1995) or single source excitation as with the APXS
(Rieder et al., 1997).

290

The operation of the XRS is as follows. The primary radiation from the XRS's
radioisotope sources excite fluorescent X-rays from the constituent elements of the
sample which are detected by a Si-PiN diode. Each X-ray deposits its energy in the
diode to produce a number of electron-hole pairs in the depleted region. The reverse

295 bias voltage sweeps the electrons towards the rear contact and the total charge is
converted into a voltage via a preamplifier that is co-mounted with the diode in the
DHA. The preamplifier collects the charge on a feedback capacitor to produce an
output pulse whose voltage is proportional to the energy of the original X-ray. This
voltage pulse is processed by the back end electronics (BEE). The signal from the
300 preamplifier has a low signal to noise ratio. The pulse shaping circuit amplifies and
widens the pulse into a shape that approximates a Gaussian. The multichannel
analyser measures the amplitude of each output pulse from the circuit and converts it
into a digital signal which is binned into one of 4096 channels according to its
amplitude. The amplitude of the pulse is directly proportional to the energy of the
305 incident X-ray. As the fluorescent X-rays are detected, they are accumulated into a
pulse height histogram over an integration time.

Analysis of the basalts using the flight spare XRS was performed with the DHA
inside a vacuum chamber at a pressure of 2×10^{-7} mbar and connected to the BEE on
310 the laboratory bench via a sealed feedthrough. The flight spare was typically operated
under vacuum, which has the same X-ray attenuation as the 6 mbar CO₂ atmospheric
conditions at Mars to within 5%. The DHA was cooled to ~250 K for standard
operation in order to reduce the detector noise on the Si-PiN diode and optimise
detector resolution. The DHA was mounted inside the chamber such that it was
315 pointing vertically downwards towards the samples. Each basalt was mounted on a
platform below the XRS which was raised until the surface of the target was flush
against the CFRP structure. The integration time for each measurement was 3 hours
which was enough time for appreciable statistics to be accumulated in the X-ray
spectrum.

320

For this study, the potassium content of the basalts were compared to analyses performed by a commercial Spectrace TN 9000 X-ray spectrometer designed for terrestrial fieldwork in order to compare the XRS with a more analytically capable instrument. The Portable X-ray Fluorescence Spectrometer (PXRF) is a field portable energy-dispersive spectrometer that has been fully characterised for terrestrial in situ fieldwork (Potts et al., 1995). It consists of two parts: a probe that contained the detector and three radioisotope sources, and an analyser which provides data acquisition, data processing and display capabilities. The instrument utilises ^{55}Fe (1800 MBq), ^{109}Cd (180 MBq) and ^{241}Am (180 MBq) radioisotope sources for primary excitation which excites the sample sequentially. The fluoresced X-rays are detected by a solid state mercuric II iodide X-ray detector with a resolution of ~ 260 eV FWHM at Mn K_{α} . The PXRF is similar in operation to the XRS although it offered considerably more flexibility for making multiple measurements on the basalt samples because it is a desktop system with considerably shorter integration times.

For the analysis using the PXRF, the basalt slabs were placed on top of the Spectrace 9000 probe aperture and primary excitation was performed by sequential illumination using ^{109}Cd and ^{55}Fe for 100s and 60 s integration times respectively.

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2.3 Argon Measurement: Gas Analysis Package

The GAP (Wright et al., 2003) was designed to perform many of the investigations associated with the exobiological goals of Beagle 2. It is capable of conducting three main studies which are (i) the search for organic matter, (ii) analysis of total light element composition and speciation and (iii) atmospheric analysis. It can analyse

345 rock, soil or atmospheric samples. Geological samples are delivered to the GAP for
analysis to one of 12 ovens mounted on a carousel, whereas atmospheric gases are
sampled passively by simply opening up one of the ovens to atmosphere. The carousel
rotates the oven containing the sample such that it is in contact with the GAP and the
sample is heated to temperatures of 1000°C. The GAP magnetic sector mass
350 spectrometer performs quantitative and stable isotopic measurements of gases
including H₂, N₂, O₂ and CO₂. The instrument can also analyse noble gases, including
Ne, Ar and Xe, as well as trace constituents indicative of extant life (such as CH₄).
The GAP uses the technique of stepped combustion to distinguish between the various
types of carbon species, including organically derived carbon, by the temperature at
355 which they burn in oxygen. Stepped combustion also allows the isotopic composition
of carbon to be measured, since the level of fractionation can discriminate between
organic and inorganic origins. As part of its broad scientific remit, the GAP can
measure the Ar isotope content of a rock and hence provide the ⁴⁰Ar measurement
necessary for K-Ar dating.

360

For the purposes of this study, the Ar isotope content was measured using a laboratory
equivalent of the GAP, called Finesse, developed in-house at the Planetary and Space
Sciences Research Institute, Open University. For the Ar measurements a 90° sector
magnetic mass spectrometer (Dennis Lee technology) was employed, which is one of
365 the constituents of the Finesse machine (Brilliant et al., 1994; Shelkov et al., 1997;
1998; Verchovsky et al., 1997; Verchovsky et al., 2002) which also includes two more
mass spectrometers: magnetic sector (SIRA 24 analyser) for carbon isotope analysis
and quadrupole (Hiden Analytical) for He, Ne and Xe measurements; all fed from a
single extraction and purification system. Ar was extracted by stepped heating of 5 to

370 15 mg of the samples wrapped in platinum-foil in the double-wall (quartz-ceramic)
furnace with a SiC heating element providing temperature up to 1400°C at which
complete release of Ar is provided. The space between the inner (6-mm diameter
quartz) and outer (ceramic) tubes is pumped by a mechanical (oil) pump. This is
important not only for preventing collapse of the quartz tube at high (>1200°C)
375 temperature, but also for significant reduction of Ar blank. The released gases were
transferred from the furnace to the cleanup section using molecular sieve at liquid
nitrogen temperature and then cleaned on the Ti-Al getter. Argon isotopes were
measured using two Faraday-cup collectors connected to the remote amplifiers with
sensitivities different by a factor of 100, which provides a wide dynamic range ($\sim 10^3$)
380 for the registration of the ^{40}Ar ion beam. Masses 36, 37, 38 and 40 were registered,
one at a time, by changing the acceleration voltage. Mass 37 is usually measured on
mass spectrometers with relatively low resolution in order to estimate the contribution
from hydrocarbon radicals on masses 38 and 36. The appropriate collector for ^{40}Ar
was chosen automatically, depending on the intensity of its ion beam. Only the high
385 sensitivity collector was used for the registration of all the other masses. The signal
intensities were measured with a high-performance multi-channel digital multimeter
(Keithley, Model 2000). The sensitivity of the mass spectrometer was calibrated using
a standard biotite with known amount of radiogenic ^{40}Ar (Afanas'ev and Zirov, 1974)
and is $\sim 8 \times 10^{-5}$ A/torr. Mass discrimination was determined using an air standard as
390 described earlier (Shelkov et al., 1998). The system blank was $\sim 2 \times 10^{-9}$ cm³ ^{40}Ar .
When the amount of Ar released is comparable with the blank, the precision of
 $^{40}\text{Ar}/^{36}\text{Ar}$ ratio measurement is $\sim 10\%$. This was the most important restriction for the
K-Ar age calculations for the samples when the amount of ^{40}Ar is low.

395 A number of performance parameters must be considered when addressing the
question of how representative the Finesse instrument is of the Beagle 2 GAP. These
include (i) the sample extraction technique, (ii) the instrument sensitivity and (iii) the
instrument blank. The radiogenic gas is extracted by stepped heating of the sample.
The finite amount of electrical power available from the Beagle 2 lander would have
400 limited the maximum temperature of the GAP ovens to ~1000-1100°C, whereas in
Finesse a temperature of 1400°C is usually used to ensure full release. In principle
this may have compromised GAP's ability to release all of the argon from a sample.
We have therefore estimated the error associated with the difference in the release
temperature between Gap and Finesse using the step heating data. The difference is
405 not significant since the maximum of ^{40}Ar release is observed at 900°C which
translates to 10% difference in the age. The Sample Analysis on Mars instrument on
MSL has ovens which have a maximum temperature similar to GAP of ~1100°C
because of power limitations. However, Park et al. (2009) found that in the case of
mars rock analogue basalts and the Zagami shergottite, that after 60 min of heating in
410 the SAM oven, ~90% of the total ^{40}Ar is released at 1100°C and ~70% of the total at
1000°C, which suggests that temperatures higher than ~1100 °C may not be required.

Should it be deemed necessary in a future mission to heat beyond the 1000-1100°C
limit of the Beagle 2 GAP, a number of further factors should be taken into account.

415 The GAP design employs a zirconium/platinum seal which should be validated for
seal integrity (including potential sticking) at further elevated temperatures. Blank
levels (which are discussed below) from the platinum oven are not anticipated to rise
unduly, though the mechanical strength of the platinum itself may degrade at such
temperatures necessitating careful trade-off between sealing force applied and

420 structural integrity of the mated assembly. Finally, it is probably inevitable that
increased oven heater power will be required, which will be limited by the capabilities
of the particular spacecraft, but this requirement may be mitigated to some extent by
additional thermal control measures to minimise losses due to conduction, convection
and radiation (only conductive losses were attended to in detail in the Beagle 2 GAP
425 application).

For mass spectrometers, the sensitivity may be expressed in terms of the current
measured at the ion beam detector as a function of the pressure of sample within the
mass spectrometer, for example in units of Amps per mbar. The Finesse laboratory
430 instrument has a sensitivity of around 0.8×10^{-4} Amps per mbar. The sensitivity of
GAP is approximately half this value i.e. 0.4×10^{-4} Amps per mbar. Both Finesse and
GAP are operated in “static” mode, in which the mass spectrometer is isolated from
the pumping system when sample gas is introduced. This increases the residence time
of the analyte gas within the mass spectrometer, with a concomitant increase in
435 analytical precision. However, because the GAP mass spectrometer has an internal
volume of approximately half that of Finesse, it requires only half as much sample gas
to achieve a given pressure. Thus, expressed in more direct units of Amps per mole of
sample gas, GAP is of comparable sensitivity to Finesse, achieving around 1 nA per
nmol of sample gas. The detection limit of Ar on Finesse is $\sim 10^{-11}$ cc. However, for
440 K-Ar dating, the detection limit of radiogenic ^{40}Ar is more relevant and is
predominantly limited by the system blank and sample contamination. The estimated
limit for the detection of ^{40}Ar is $\sim 10^{-10}$ cc, although this figure does not necessarily
translate to the minimum quantifiable limit which is higher.

445 The analytical “blank” is the signal that would be measured by an analytical system in
the absence of any deliberately introduced sample. When aiming to analyse argon in
terrestrial laboratories, it is important to exclude terrestrial atmosphere from the
system, as air contains ~1% argon. Finesse is therefore built from ultra-high vacuum
components and utilises getters to further reduce the argon blank. GAP was designed
450 around similar principles, and has the advantage that although argon constitutes of
order 1% of the martian atmosphere, the absolute pressure of argon is around 15 times
lower than that on Earth, resulting in reduced absolute leak rates into the GAP
vacuum system. Overall the argon blank of GAP on Mars is still to be determined, but
could in principle be designed to be similar to that of Finesse.

455

3. Results & Discussion

The collated results for the analysed potassium content, the ^{40}Ar content, and the Ar-
Ar and K-Ar ages for the basalt samples are given in Table 1. The uncertainty on the
460 potassium measurement by the PXRF and Beagle 2 XRS was derived from
comparison of analyses of geochemical reference materials with certified
concentrations (Talboys, 2006). The K measurement for sample E for the PXRF is an
average of four measurements on the surface of the slab (two on each side). The
analysed ^{40}Ar content for each sample was corrected for atmospheric ^{40}Ar
465 (McDougall and Harrison, 1999). The uncertainty on the K-Ar ages were derived
from and limited by the uncertainties on the respective K and ^{40}Ar measurements and
are quoted to the one sigma level. The uncertainty on the Ar-Ar age measurements are
quoted to the two sigma level. Since the K-Ar uncertainties are typically an order of

magnitude higher than the Ar-Ar ages then quoting the latter ages to one sigma makes
470 no difference to their comparison.

In general, the K-Ar ages for samples A (255 ± 84 Ma) and B (186 ± 63 Ma) agree with
their Ar-Ar ages, within their uncertainties although the Ar-Ar age for sample B is not
well constrained and within the range 180 - 500 Ma. The K-Ar ages for samples C
475 (109 ± 28 Ma) and D (88 ± 30 Ma) are lower than the corresponding Ar-Ar ages (at
179 Ma and 183 Ma respectively) and underestimated by a factor of two. The K-Ar
age for sample E was higher than the Ar-Ar age but both ages still broadly agree. The
superior accuracy of the PXRF compared to the XRS is reflected in the smaller
uncertainties of the ages derived from the PXRF. The average uncertainty for the K-
480 Ar ages with the K measurement made by the PXRF was $\sim 20\%$ although the
uncertainty on individual measurements has a considerable variation, as Table 1
shows. Doran et al., (2004) argues that, given how poorly constrained the absolute
ages of martian geological units are, a 20% uncertainty on the K-Ar age would be of
scientific use. The accuracy of the individual K and Ar measurements are the biggest
485 source of uncertainty for the derived age and clearly advances in the analytical
performance of similar instruments for deployment on planetary surfaces are
important.

A younger K-Ar age for samples C and D can not easily be attributed to argon loss
490 since the Ar-Ar dating demonstrates that the samples did not suffer wholesale argon
loss. There remains the possibility that some portion of the samples suffered alteration
in some areas selected for the Ar analysis on Finesse but this is not very likely.

Sample grainsizes were reduced for analysis in Finesse and argon loss can also occur

during sample preparation from excessive grinding, but again this is not likely to have
495 been caused by gentle hand grinding. Another possible reason may be due to
systematic errors introduced as a result of the low level of ^{40}Ar occurring close to the
limit of reliably determining the concentration (as opposed to the limit of detection) of
the mass spectrometer.

500 **4. Operational Considerations for In situ K-Ar Radiometric Dating on Mars**

In this section, we discuss the operational constraints and considerations to
performing a radiometric date measurement on Mars. Whatever the payload
configuration, choice of measurement target is important. From a field geologist's
point of view, exposed bedrock is generally more preferable compared to loose
505 boulders. Previous landing sites on Mars have provided access to "grab-bag" samples
(VL1, VL2, MPF and MER-Spirit), exposed bedrock (MER-Spirit, MER-
Opportunity), sedimentary lithologies (MER-Opportunity) and erratics (MER-
Opportunity). Clearly, mobility (for detection and access) and dexterity (for
measurement and sampling) are key variables.

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Static landers, with zero mobility and limited dexterity, are heavily dependent on
landing position and hence are unlikely to encounter bedrock within reach of the
deployable payload. Boulder fields (VL1, VL2, MPF and MER-Spirit (plains)) could
yield interesting targets from an array of samples but origin may be ambiguous.

515 Rovers (moderate mobility and moderate dexterity) provide an ideal platform for
identifying and accessing outcrops or sub-crops. The latter may be possible with
suitably equipped rovers such as ExoMars (ground penetrating radar (~3 m) and

sampling drill (~2 m)). All situations however are subject to accessibility and constrained by platform and payload engineering.

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Once targeted, rocks would need to be prepared using a grinding tool to ensure the measurement footprint is suitably sized (~22 mm in the case of the XRS), flat and fresh material (if present) is exposed. The Rock Abrasion Tool (RAT) on MER-Spirit and MER-Opportunity (Gorevan, 2003), or something akin to it, would serve this purpose. Unfortunately, the so called Rock Corer Grinder (RCG) fitted on the Beagle2 PAW (Pullan, 2004) was not designed to provide the same function so XRS measurements would have been restricted to unprepared, inevitably rough and probably contaminated (i.e. non-fresh) materials (Fig. 2). Contact measurements using the XRS on an RCG prepared surface would have been avoided. As a consequence there would have been no guarantee that the XRS and GAP measured the same material or whether it was in the same state. This is an important operational consideration for future applications since it could have been particularly detrimental to any radiometric results obtained. The RCG was however designed to acquire cores from the fresh interior of rocks and deliver them to the GAP via an inlet port. A key measurement for radiometric dating is determining the mass of the sample analysed by the GAP in order to convert the number of atoms of ^{40}Ar into the fractional mass required to calculate the age. On Beagle 2, an estimate of the mass of a sample delivered to the GAP would have been obtained visually. The GAP inlet mechanism consisted of a shelf onto which the sample was deposited before committing to an oven. Sample volume would have been determined using the stereo camera in macro mode (close-up lens filter) and illuminating the inlet recess with an LED. Sample mass would then have been derived following in situ assessment of the composition

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from elemental chemistry (XRS) and mineralogy (Mössbauer) of the host material. It is difficult to estimate the uncertainty of the sampled mass, although trials using the flight spare RCG sampling various geological materials would have constrained this uncertainty.

An alternative to in situ measurement might be an integrated XRS within an on-board laboratory. One benefit of this is that the same material is analysed by both the GAP and the XRS. This would require suitable core samples on which to perform geochemical analysis prior to analysis with the GAP. The advantage of analysing core samples is that they can be extracted from deep within rocks or exposures at a depth beyond the weathering or alteration zone (if such an interface exists and is reachable on Mars). One potential drawback for radiometric dating is the quantity of material obtained since selective sampling bias may occur if the target material is coarse, heterogeneous and/or brecciated (as opposed to fine, homogenous and/or massive).

Aside from the sampling strategies, the K measurement by the XRS is subject to several field effects. Firstly, surface roughness may alter the relative X-ray fluorescence intensities from various elements. A correction for the effect of surface roughness for the in situ analysis of rocks by a field portable X-ray spectrometer has been developed by Potts et al. (1997a). Ideally a sample preparation tool could be utilised to make the surface flat such as the aforementioned RAT which was capable of making a 'crater' of dimensions 45 mm in diameter and depth of 5 mm on the rock (Gorevan et al., 2003). Another effect is sample inhomogeneity from the natural mineralogy which may produce a variation of the K content (Potts et al., 1997b). This can be solved using multiple measurements on the sample to determine an average

composition. In addition, multiple measurements of Ar would also be useful. Finally, rocks may have a weathered coating such that the geochemical composition of the exterior differs from the interior (Potts et al., 2006). This can again be addressed by use of a sample preparation tool to remove the weathered surface.

To perform an accurate measurement of the radiogenic Ar in situ on Mars, the sources of non-radiogenic Ar and methods of argon loss must be taken into account (as considered by Swindle, 2001). Weathering processes on the surface of the rock can alter the Ar content (McDougall and Harrison, 1999) which is the reason why a fresh interior portion of the rock is sampled. Argon loss occurs by heating in the rocks' history to a temperature high enough to liberate the Ar and this is a common mechanism for Earth rocks (McDougall and Harrison, 1999). When a rock is heated to such a high temperature it undergoes metamorphism where its physical and/or chemical properties change. Swindle (2001) maintains that few rocks on Mars will have experienced metamorphism and so argon loss by this method is unlikely. Impact heating is another mechanism for argon loss but the process only heats a small fraction of rocks to a sufficient temperature. For Mars the main sources of non-radiogenic ^{40}Ar are mainly from the atmosphere and in magma. For terrestrial rocks, any ^{36}Ar present is assumed to originate from the Earth's atmosphere and accompany ^{40}Ar in the ratio 296. On Mars, this ratio is not well characterised and is in the range 1700 – 1900 (Bogard and Garrison, 1999). However, any instrument similar to GAP would have constrained this value. There is an additional component of ^{40}Ar in the magma with an $^{40}\text{Ar} / ^{36}\text{Ar}$ ratio of 200-400 (Bogard and Garrison, 1999). A further complication is that where all ^{36}Ar in Earth rocks can be assumed to come from the atmosphere, in the case of Mars it can also be produced by high-energy cosmic ray

interaction with the regolith. However, another Ar isotope, ^{38}Ar , is produced by cosmic rays and the ratio $^{38}\text{Ar} / ^{36}\text{Ar}$ is expected to be present in a fixed ratio and so
595 the cosmogenic ^{36}Ar can be derived. Ar-Ar dating has superseded K-Ar dating in geochronology laboratories because it can provide more accurate and precise crystallisation ages and circumvents the problem of radiogenic Ar loss.

Studies of the martian meteorites have shown that their K-Ar ages all generally agree with the Ar-Ar age with the exception of ALH84001 where an impact resetting event
600 probably occurred at ~ 4 Ga ago (Doran et al., 2004) which suggests that non-radiogenic argon and argon loss had not generally occurred. However, recent studies of the Zagami shergottite have shown that it contains a significant magmatic contribution of non-radiogenic ^{40}Ar (Bogard and Park, 2008a). Therefore, a challenge for in situ K-Ar dating is to determine whether analysed samples contained large
605 amounts of excess magmatic ^{40}Ar . An isochron dating analysis is a useful method of determining if excess Ar is present in the sample which essentially involves plotting the potassium content versus the total (radiogenic and non-radiogenic) ^{40}Ar . This analysis when applied to shergottites, including Zagami, showed that similar amounts of excess ^{40}Ar were inherited from the magma during their crystallization. A similar
610 analysis of nakhlites showed that they contained essentially no excess argon (Bogard and Park, 2008b). Therefore, an isochron analysis could be applied when performing robotic in situ dating provided a sufficient range of K contents can be analysed so as to define the isochron slope (Bogard, 2008c).

615 **5. Summary / Conclusions**

The aim of this study was to investigate the feasibility of in situ K-Ar dating using robotic payloads on Mars. K-Ar dating was achieved on five basalt slabs using the flight spare model of the XRS, for the potassium measurement, and a laboratory analogue of the GAP for Ar. Both of these techniques were similar in operation and analytical performance to the Beagle 2 flight models. The measurements were performed on martian analogues that had similar ages and K and ^{40}Ar contents to martian shergottites and nakhlite meteorites. The K-Ar ages were compared against complementary Ar-Ar ages. The K-Ar ages were found to broadly agree with the Ar-Ar ages although where discrepancies arose these were a result of the ^{40}Ar content being near the detection limit or an inhomogeneous distribution of K.

Given the preliminary results, we can conclude that in situ radiometric dating is possible in principle although with the following caveats:

- (1) Careful attention must be paid to improving the analytical performance of the instruments, in particular the accuracy and detection limits. The accuracy of the K and Ar measurements are the biggest source of random uncertainty in the derived K-Ar age.
- (2) Multiple measurements must be made on rocks to establish a bulk composition and account for heterogeneities.
- (3) Careful attention must be made to sample acquisition.
- (4) Given the number of variables involved in successfully performing a radiometric date measurement on Mars, further work needs to be performed to characterise this technique for robotic elements in terms of the instruments employed, sampling strategies, analytical procedures and tools, on a wider variety of martian analogues.

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Figure Captions

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Fig. 1. The Detector Head Assembly of the XRS with constituent components labelled. The aluminium ring on the CFRP cap is not shown.

Fig. 2. The Rock Corer Grinder (RCG) on Beagle 2 was capable of sampling some
845 rocks but had a small grinding footprint (dictated by the 10 mm head diameter, shown here for scale). In addition, both the tool and PAW lacked the capability to remove the residual debris mound that was produced. Subsequent contact between this positive feature and the XRS detector head would have probably resulted in contaminating the source capsules and/or potentially compromising the Be window. Examples shown
850 are orthoquartzite (left) and massive basalt (right). Both samples have oxidised weathering/alteration rinds and produce debris mounds in excess of 5 mm high.

Table 1.

Basalt Sample Identity	K Content (%)		⁴⁰ Ar content	Radiometric Ages		
	Beagle 2 XRS	PXRF		GAP (cc/g)	Ar-Ar (Ma)	K-Ar (Ma)
			B2 XRS			PXRF
A	0.28±0.07	0.26±0.03	$(3.0±0.3)×10^{-6}$	187.8±2.8	255±84	273±70
B	0.63±0.16	0.57±0.06	$(4.8±0.5)×10^{-6}$	180 - 500	186±63	204±52
C	0.41±0.10	0.45±0.05	$(1.8±0.2)×10^{-6}$	179±3	109±28	99±14
D	0.36±0.09	0.44±0.05	$(1.3±0.1)×10^{-6}$	183.25±3.6	88±30	72±19
E	0.24±0.06	0.33±0.04	$(2.5±0.2)×10^{-5}$	1141±23	1627±289	1308±146
F	0.24±0.06	0.19±0.02	<DL	187.4±2.7	-	-

Table 1. Tabulated results comprising K content as measured by the PXRF and

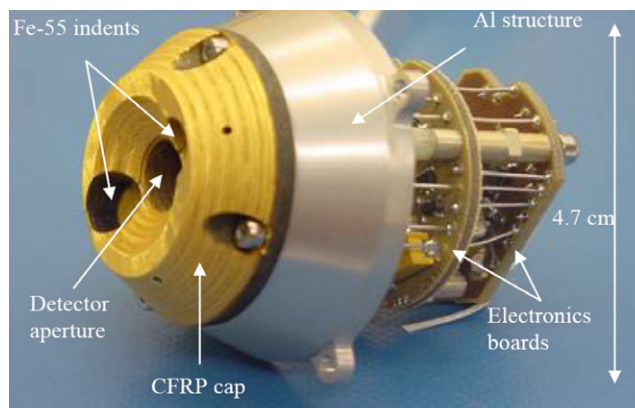
Beagle 2 XRS, ⁴⁰Ar content as measured by flight-like version of the GAP and

855 radiometric ages as derived using the Ar-Ar and K-Ar techniques. Each K-Ar age
corresponds to a K measurement as measured by each of the X-ray Spectrometers.

The sample identities assigned by Dept. of Earth Sciences, Open University are as
follows: A: Z1865.1, B: Z1868.18, C: Z1853.6, D: Z1873.25, E: Z1866.1, F:

Z1862.16.

860

Fig. 1.**NOTE: Please reproduce as colour for the web and greyscale for print.****Web:**

865

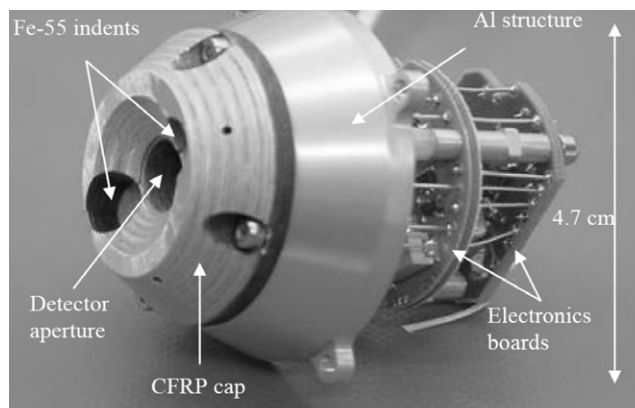
Print:

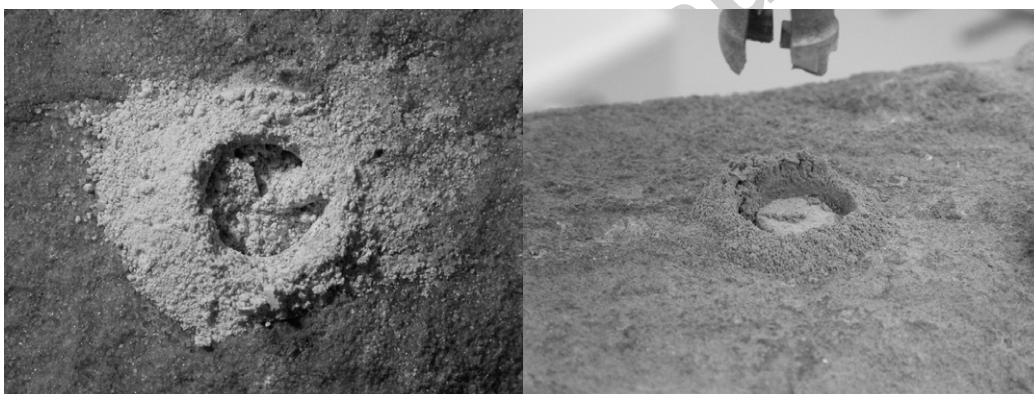
Fig. 2.

870 **NOTE: Please reproduce as colour for the web and greyscale for print.**

Web:



Print:



875